INORGANIC CHEMISTRY

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FIRST STAGE
INORGANIC CHEMISTRY.

BY

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PREFACE.

The importance of the actual performance of experiments in the study of chemistry is now generally recognized. It is, however, quite possible for a student to work diligently through a course of preparations in the laboratory and yet not acquire the power of interpreting the observations he may make, or of deducing from them the principles to which they point.

We have therefore thought it desirable, in the earlier chapters, to give some idea of the field of investigation, and of the methods employed by the chemist in conducting his inquiries.

The subsequent study of the elements and their compounds may be regarded as affording additional illustration and extension of the fundamental principles there laid down.

The attention having been thus clearly directed to the aims and purposes of the study of chemical science, interest in the systematic part of the book will be fully maintained, and the true value of experiment as an instrument of scientific research will be appreciated.

The contents of the treatise have been arranged to meet the requirements of the Science and Art Department for the Elementary Stage, though for the sake of continuity, some of the subjects have been rather more fully treated than the Department Syllabus would seem to demand.

A summary has been appended to each chapter that the student may use as a *précis* for the purpose of reviewing or recalling the contents of the chapter.

The assumption is made throughout, that the book is used as a companion in the laboratory, and hence figures of apparatus are only given in cases where some aid was thought to be needed in the arrangement or fitting of the apparatus. The same remark applies to the description of the experiments that are to be performed by the student.

November 1896.

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FIRST STAGE CHEMISTRY.

CHAPTER I.

DEFINITION AND AIMS OF CHEMISTRY.

The dawn of chemistry.—From very early times the constitution of matter has been a subject of interest to man. The first investigators were satisfied with observations almost entirely confined to the colour, hardness, or other physical properties of the mineral substances which they found around them ; and whenever they succeeded in bringing about any transformation of these substances, the process by which the change was accomplished received little attention.

Thus iron, copper, and a few other metals were obtained, but by empirical methods. Substances chemically identical, such as water and steam, were regarded as essentially different, whilst other substances—for instance, ice and quartz—though composed of entirely different materials, were, in consequence of their similarity in appearance, regarded as being forms of the same substance.

In the investigation of natural phenomena it is always necessary in the first place to perform experiments. Experiments carefully planned were, however, almost unknown in the beginnings of chemistry, and even when performed, the deductions drawn were too often falsified through placing a too great reliance on what, judging by the *appearance*, the resultant body might be. Thus Geber, by adding mercury to lead, obtained a silver-white solid which he regarded as being tin, which indeed it resembles.

Experimental inquiry.—Solid progress in the knowledge of chemistry has been achieved only after the performance of a vast number of experiments, each experiment being rigidly followed up by others, and the conclusion only accepted when the evidence accumulated from every possible source places it beyond dispute.

As an instance of the methods followed in the chemical investigation of matter, let us take cylinders (A) containing oxygen, and (B) containing carbon dioxide. So far as we can see they are similar, but if we perform varied experiments we shall learn something of the chemical differences between the gases.

Exp. 1.—Pour clear lime-water into each ; in A no change is observed, in B the lime-water becomes turbid.

Exp. 2.—Place a lighted taper in each ; in A the taper continues to burn, and burns even more brightly than it does in air ; in B the taper is extinguished.

How the composition of matter is investigated.—The science of chemistry is essentially and primarily devoted to the determination of the composition of matter, and this subject is therefore one of the greatest importance to the chemist.

In the desire to ascertain the composition of a complex substance, we use means whereby it may be broken up into simpler forms, and we may further cause these simpler parts (where possible) to unite again so as to reproduce the original substance.

Exp. 3.—Break up about 2 grammes of calcite into small fragments, and introduce it into a tube of infusible glass[1] fitted with a cork and delivery-tube as shown in the figure. Heat the lower part

---

[1] Weigh the tube and contents before and after the experiment. *E. g.*—

Weight of tube and calcite	25·34	grms.
,, ,, only	23·25	,,
,, calcite	2·09	,,
,, tube and contents after heating	24·50	,,
,, residue	1·25	,,
Loss of weight during heating, *i. e.* carbon dioxide	0·84	,,

of the tube as strongly as possible in the flame of a large Bunsen burner, or better still, in the flame of a blowpipe.[1]

A gas will be given off, and may be collected in a small test-tube over water. Continue the heating for about half-an-hour, but in the meantime examine the gas that has been obtained.

It will be found to show the properties already described under Exps. 1 and 2 as those belonging to *carbon dioxide.*

The residue in the tube is allowed to cool, and is then moistened with about 5 c.c. of water. It will be noticed that the liquid becomes warm (calcite when thrown into water does not develop heat), and by pouring on it more water, say 100 c.c., some of it dissolves[2] (calcite does not dissolve in water). The residue in the tube is evidently no longer calcite ; the properties observed are those belonging to the body known to us as *lime.* By heating calcite we have obtained from it lime and carbon dioxide.

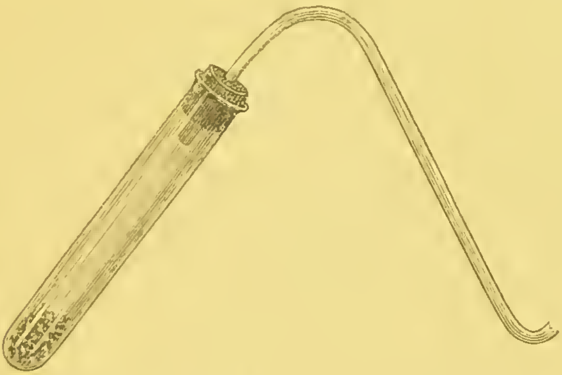

FIG. 1.

Exp. 4.—Now decant off the clear solution mentioned above, and shake it up with some of the carbon dioxide, or expel air from the lungs through it. It will become turbid and deposit a white powder. If this white powder be collected and dried it will be found to possess the essential characters of calcite, and if heated, it will give off carbon dioxide, and leave, as a residue, lime.

---

[1] Similar results may be shown with magnesite, and this mineral possesses the advantage of undergoing decomposition more readily.

[2] That something has dissolved may be shown by evaporating a little of the water to dryness and noting that a solid residue is obtained.

The former experiment affords an example of the method of investigating composition by separation into simpler constituent parts, *i. e.* by *analysis*, and the latter that of reproducing a substance by bringing together the constituent parts, *i. e.* by *synthesis.*

How the chemical identity of two substances is established.—From these experiments we also gather that two substances are regarded as identical from a chemical point of view when on being exposed to heat or other agencies, or to the action of chemical re-agents, they exhibit like changes of composition. This being the case then, notwithstanding certain differences of outward appearance, texture, and cohesive power, we regard calcite[1] and the white powder above mentioned as *chemically identical* substances. Similarly lampblack and diamond, though as unlike in form, hardness, and colour as two substances well can be, are yet chemically identical. For if we burn lampblack and diamond in a sufficient supply of oxygen, the product in both cases consists entirely of carbon dioxide. Also if we burn equal weights of lampblack and diamond, the weight of the carbon dioxide formed in the one case is precisely the same as that formed in the other. Changes of composition brought about by the action of chemical agents on lampblack in all cases correspond to those effected on diamond, and the chemical identity of lampblack with diamond is thus established.

Physical properties of matter as distinguished from chemical properties. — Properties such as lustre, hardness, tenacity, and state of aggregation, are classed as purely *physical;* they affect matter according to the circumstances of pressure and temperature, etc., under which the body exists, and as these alter, so the physical state or condition of the body is liable also to alter. *This change of physical state is not accompanied by change of weight or composition.* The distinction between the physical and chemical changes in matter is of such importance that we append other examples which serve to throw light upon it.

Exp. 5.—A small fragment of iodine is placed in a test-tube and gently warmed; presently, violet vapours rise, and the whole of the iodine may thus be volatilized. At the upper (cold) part of the tube the vapour cools down, and there is formed a deposit of black crystals.

---

[1] Marble and crystals of aragonite may be examined by the student, these being also chemically identical with calcite.

Whatever further experiments we perform with this deposit will only lead to the conviction that it is chemically identical with the fragment of iodine originally taken, a conclusion which is strongly supported by the fact that (provided none of the violet vapour has been allowed to escape) the weight remains unaltered. The change which has taken place is a purely physical one, the solid iodine having been transformed into vapour of iodine, and condensed again on cooling to solid iodine.

Exp. 6.—Heat a piece of platinum wire in the flame of a Bunsen burner; it glows brightly, and for the time being loses the colour and to a large extent the tenacity of platinum. On withdrawing it from the flame and allowing it to cool, its original colour and character return.

Its properties will be found to have undergone no change, its weight likewise is the same as it was before it was heated. As in the case of the iodine, the high temperature of the flame has merely brought about a physical change of a temporary character.

Exp. 7.—Hold with the forceps an inch or so of magnesium ribbon in the flame. This likewise glows at first, but almost immediately gives out a dazzling light which will continue even after the ribbon is withdrawn from the flame.

When the light dies down, we see, not the original ribbon, but a white film retaining perhaps the form of the ribbon, but no longer the grey lustre of the metal; instead of a tough metal that may be bent, the residue is fragile in the extreme, and crumbles as it is touched. Furthermore if a fragment of this be again introduced into the flame, it may glow, but no longer gives out the dazzling light, and on removal from the flame it cools and resumes the white filmy appearance once more. Something more than a temporary change of physical character is indicated here. Finally, although the white powder is so light and flimsy, yet if it be all collected, as may with care be done by heating magnesium in a small porcelain crucible, it will be found that the resulting powder is heavier than the ribbon originally taken.

Lead, zinc, tin, iron, and many other metals, when heated in air, likewise undergo change of chemical composition with increase of weight, and by suitable means it can be shown that the increase in weight is due to the combination of oxygen (of the air) with the metal during the course of the heating.

As a last instance, let us consider the case of a gas—hydrogen. If this gas be heated it expands very much in the same degree as other gases do, if it be cooled or subjected to pressure it contracts, if it diffuses it does so in obedience to a law which applies to all gases. Being a gas, it behaves as a gas, and in the above respects all normal gases agree, whatever their chemical nature may be; the changes which ensue are temporary, and vary with the surrounding conditions. They belong to the region of physics.

But now burn the hydrogen, and water vapour is produced (see Chapter VII.). The product is heavier than the hydrogen from which it is obtained, it condenses readily to a liquid (water) at ordinary temperatures, the property of inflammability has disappeared, and we are satisfied that hydrogen and water vapour are different chemical substances. A *chemical* change has been wrought.

Elements and compounds.—We have seen that certain substances, and in fact the very great majority of substances commonly met with, are of a complex character, so that by employing the resources at the disposal of the chemist they may be decomposed or broken up into simpler substances. This process of decomposition may perhaps not end here, for by more powerful agencies it may be found possible to break down these simpler parts still further. Thus, we may resolve a body into constituent parts, A and B, showing different chemical properties, but A may be capable of further resolution into a and a^1, B may be capable of further resolution into b and b^1.

If such a process be carried far enough, we ultimately arrive at products which no known methods or agencies are capable of resolving further; that is, so far as experimental evidence avails us, the conclusion must be drawn that we have now before us bodies which in all their parts possess the same chemical properties, Substances of this nature are termed *elements*, and a substance consisting of two or more elements combined together is termed a *compound*.

Definition of chemistry.—Summing up we may say, then, that the aim of the chemist is—

(1) To decompose complex matter (compounds) into simpler forms, so long as the resulting bodies show properties differing chemically from the original substance, the ultimate products of such decomposition (elements) being no longer capable of further resolution by any known method.

(2) To ascertain by means of experiment the properties of elements and compounds, so far as they are associated with differences of chemical composition, and to study the manner in which they react upon one another.

(3) By means of the analytical method employed in (1), and by the synthetical method in (2), to trace the steps in the transformations which take place, so as to express the relations which exist between a compound body and its constituents.

(4) To study the nature of the attraction by which the different constituents of a compound body are held together in chemical combination, and the conditions which influence this attraction.

General methods employed in bringing about chemical change.—When a substance is heated, the changes first observed are usually physical in their nature. The substance expands, or it undergoes an alteration from the solid to the liquid condition, or from the liquid to the gaseous. Such changes betoken a passage to a state in which the particles of the body become more free to move; or in other words, the cohesion of the particles is diminished. As the temperature is raised, even the chemical attraction which has previously held together the different chemical constituents of the body is wholly or in part overcome, and the body is decomposed. Given a sufficiently high temperature, most compound bodies undergo decomposition.

Secondly, substances which conduct electricity may often be readily resolved into their more elementary parts by means of the electric current.

Thirdly, the simpler constituents of a body may be liberated by intimate contact with another chemical substance, the reaction being facilitated by heat.

Chemical symbols.—The description of the composition of a body, and of the changes which it undergoes under different circumstances, is of so frequent occurrence in chemistry that it has been found convenient to use abbreviated forms or symbols to indicate the ultimate elements of which all known substances are composed. The symbols employed to designate them usually consist of the initial letter or significant letters of the name of the element.

The number of bodies at the present time recognized as elements is about seventy. Improved methods and appliances are however constantly being brought into use; also discoveries in other branches of science are the means of presenting matter to us in new forms and of placing more powerful agencies at the disposal of the chemist. Substances which we now believe to be elements may thus be proved to be compounds, while other bodies, of which we now think the exact composition has been ascertained, may probably be found to contain elements hitherto unrecognized.

The list on page 9 shows the symbols used, and also the atomic weights of the more common elements.

The symbol is, then, the abbreviation for the name of an element. But it signifies more than this, for whenever two or more symbols are used in regard to chemical transformations, they imply not only the elements by name, **but also definite weights of the elements**, bearing the same relation to one another as the atomic weights, and a number placed in juxtaposition to the symbol indicates a multiple of these weights. Thus Hg and I_2 imply that the mercury and the iodine are to be taken in the proportions 198·8 and (125·9 × 2).

Formulæ.—When two or more symbols are placed in immediate juxtaposition, it is implied that the elements represented are in a state of combination in the relative quantities indicated. Thus HgI_2 stands for a compound of mercury and iodine, the red iodide of mercury, and H_2O for a compound of hydrogen and oxygen, water.

Equations.—The sign + placed between two or more

THE SYMBOLS AND ATOMIC WEIGHTS OF THE MORE COMMON ELEMENTS.[1]

Hydrogen	H	1·00
Carbon	C	11·9
Nitrogen	N	13·95
Oxygen	O	15·88
Fluorine	F	18·96
Sodium	Na (Natrium)	22·88
Magnesium	Mg	23·8
Aluminium	Al	26·9
Silicon	Si	27·9
Phosphorus	P	30·8
Sulphur	S	31·8
Chlorine	Cl	35·18
Potassium	K (Kalium)	38·85
Calcium	Ca	39·7
Chromium	Cr	52·2
Manganese	Mn	54·7
Iron	Fe (Ferrum)	55·6
Cobalt	Co	58·3
Nickel	Ni	58·3
Copper	Cu (Cuprum)	62·9
Zinc	Zn	64·5
Arsenic	As	74·5
Bromine	Br	79·36
Strontium	Sr	86·84
Silver	Ag (Argentum)	107·12
Cadmium	Cd	111·1
Tin	Sn (Stannum)	116·8
Antimony	Sb (Stibium)	119·0
Iodine	I	125·9
Barium	Ba	136·2
Mercury	Hg (Hydrargyrum)	198·8
Lead	Pb (Plumbum)	205·4
Bismuth	Bi	206·3

---

[1] The atomic weights have been recalculated according to the more recent data regarding the atomic weight of oxygen and the density of hydrogen.

elements or compounds indicates that the bodies in question are brought together under such conditions that they may react upon one another; and the sign =, that when they have so reacted, the resulting products are those placed to the right-hand side of the sign =. Thus $Hg + I_2 = HgI_2$ indicates that mercury and iodine are brought together in such a condition that they act upon one another in the chemical sense, and that they form the red iodide of mercury indicated by HgI_2; and further, that the quantities which take part in the reaction, and which go to form the compound HgI_2, are in the relative proportion already spoken of.

Metals and non-metals.—Had we before us specimens of each of these elements we should find that a large number of them, such as silver, gold, lead, exhibit the following general characters—

Physical:

(1) They reflect light well, especially at a polished or freshly cut surface; in short, they possess a pronounced lustre.
(2) They are capable of being hammered into plates or drawn into wire; in other words, they are malleable and ductile.
(3) They have usually a high specific gravity.
(4) They are good conductors of heat and electricity.
(5) They are volatilized, as a rule, only at very high temperatures.

Chemical:

(1) When dissolved in mineral acids, hydrogen is evolved.
(2) When exposed to air or oxygen, especially when heated, they usually lose their brightness of surface and become dull.

On the other hand, there are about a dozen elements, such as oxygen, bromine, and sulphur, (printed in thick type, page 9,) which stand in marked contrast to the above. They are under ordinary conditions gases, liquids, or solids possessing very little tenacity. Those, such as carbon, silicon, and iodine, which are solids, are therefore brittle, and though in the crystalline form they reflect light from their smooth surfaces, there is an absence of the peculiar lustre observed in the metals.

They are moreover bad conductors of heat and electricity, and when heated they, as a rule, are either gases or are transformed into the gaseous condition at comparatively low temperatures. Chemically they are characterized by being either unacted upon or only feebly acted upon by mineral acids or by oxygen. It is usual therefore to recognize these broad differences by subdividing the elements into two classes, the former being termed the *metals*, and the latter the *non-metals.*

SUMMARY.

1. Chemistry is the science which relates to the composition of matter, the changes of composition which it undergoes, and the phenomena which accompany these changes.
2. The composition of matter is investigated—
   (*a*) by decomposing complex substances (analysis);
   (*b*) by building up complex substances again from their simpler constituents (synthesis).
   As an instance, take calcite.
3. The *physical* properties of matter must be held distinct from the *chemical* properties. The former may change as the surrounding conditions (temperature, pressure, etc.) change, and without any accompanying alteration of weight or composition; but change in chemical properties is associated with change of weight and composition.
   Illustrative examples—iodine, platinum, magnesium, and hydrogen.
4. The *element* is the product obtained when further decomposition is no longer capable of being effected.
5. The operations of the chemist and the chief resources at his disposal.
6. The use of symbols for the purpose of expressing the facts and phenomena of chemistry.
7. The distinction between *metals* and *non-metals* by reference to—
   (*a*) specific gravity, colour, lustre, tenacity (physical properties);
   (*b*) readiness of combination with oxygen, chlorine, etc., and stability of compounds so formed (chemical properties).

QUESTIONS.—CHAPTER I.

1. What is limestone, and how is it converted into lime?
2. The composition of a body may be determined by *analysis* or by *synthesis;* explain these terms, and give examples in illustration of your answer.
3. Define the terms *element* and *compound.* Why do we regard oxygen as an element and marble as a compound?
4. What properties of matter do you define as *physical* properties, and what as *chemical* properties?
5. Describe carefully the changes which take place when (*a*) iodine, (*b*) magnesium are strongly heated in air.
6. State in separate paragraphs (*a*) the physical, (*b*) the chemical properties of any element or compound you choose.
7. What are the principal agencies by which chemical decomposition is effected?
8. Give the precise meaning to be attached to the symbols H, H_2O, HgI, HgI_2.
9. Write out in separate columns the properties that are generally characteristic of (*a*) metals, (*b*) non-metals.
10. What are the objects that a chemist has in view in his investigation of matter?

CHAPTER II.

THE NATURE OF CHEMICAL REACTION.

When two or more bodies react upon one another, it is desirable to conduct an inquiry not only into the qualitative nature of the change, but also by weighing and measuring to determine the quantities of the materials which have taken part in or resulted from it. The former of these steps involves a knowledge of the properties of the reacting bodies, and a determination of those resulting from the reaction; the latter is effected by the process of estimating the amount of each of the bodies concerned with the aid of the balance. The necessity for adopting both these courses of procedure will be evident when we have considered the matter in greater detail. For the present we shall, as a prelude to such consideration, follow the changes which take place as actually observed in some simple instances.

Exp. 8.—Having weighed out 15·8 grammes of mercury and 10 grammes of iodine, rub them intimately together in a mortar,[1] it will be observed that the mercury, and at the same time the iodine, both gradually lose their characteristic appearance, and in place of them we have a powder every particle of which is green and amorphous. The product shows none of the characteristic properties of either mercury or iodine.

---

[1] The operation is facilitated by adding a few drops of alcohol, also smaller quantities of the substances may be used, provided the same proportion is preserved.

Exp. 9.—Add a further quantity of 10 grammes of iodine, and bring this into intimate contact with the green powder, and it will be transformed into a red powder, the iodine as such disappearing. In this case also all the particles of the red powder will be found to possess the same character.

Exp. 10.—Again add 10 grammes of iodine, and perform a similar operation. On carefully examining the resulting substance, we shall be able now to discern two kinds of particles, and by *gently* warming, or by solution in alcohol, the whole of the iodine added in this experiment may be extracted, while in the case of the green or red powder, it is no longer possible to extract the iodine by such means.

In the first two experiments the mercury and the iodine have undergone a process quite different from any ordinary admixture, since they no longer exist in the free condition, and they are held together by a force different in character from ordinary cohesion. The phenomena are those which accompany *chemical combination*, and the mercury and iodine are bound together in the compounds formed, by *chemical attraction.*

In this, as in all other chemical reactions that we are acquainted with, it is necessary that the substances between which the reaction takes place shall be brought into intimate contact, and we learn therefore that before chemical reaction can take place, *there must be contact between the particles.* Chemical attraction is therefore unlike gravitation or magnetism, for these forces can be exerted over measurable distance.

Had we taken, in the first experiment, a smaller quantity of iodine relatively to the mercury, we should have had some of the mercury remaining uncombined, just as iodine remained uncombined in Exp. 10. We might have proceeded by trial to determine what proportions of the mercury and iodine must be used in order to form the green or the red powder respectively, without excess of mercury or of iodine.

Had we done so, we should have arrived at numbers bearing the same relation to one another as the quantities actually employed in Exps. 8 and 9. We learn, therefore, that 1·58 grammes of mercury combine with 1 gramme of iodine to form the green substance, and with 2 grammes to form the red substance, and that chemical combination takes place in these proportions.

But on examination, the relation 1·58 : 1 will be found proportional to the atomic weights of mercury and iodine, and we may therefore represent the chemical reaction which has taken place thus—

$$Hg + I = HgI;$$

and the result of the second experiment may be expressed—

$$HgI + I = HgI_2;$$

and of the third—

$$HgI_2 + I = HgI_2 + I,$$

no change having taken place.

We have then, above, an instance of chemical combination by contact alone. It is, however, much more usual to find that chemical action is not set up until the reacting bodies are brought into much more intimate contact than is possible by mechanical admixture. Thus, it is promoted by *heat*, which brings the particles of the reacting bodies into a more mobile condition, and even vaporizes them; or by *solution*, which acts similarly. In either case a very much greater freedom of the particles is effected, and this brings about more intimate contact, and assists chemical reaction in a very remarkable degree. To illustrate this, and to afford a further example of chemical change by combination of elements, we shall consider the behaviour of iron and sulphur.

Exp. 11.—Mix together 17·5 grammes of iron filings and 10 grammes of flowers of sulphur; a greenish-looking powder results, but both the iron and the sulphur can be seen in it by means of a magnifying-glass; moreover, a magnet will extract the particles of iron, and the sulphur will remain, both unchanged—mere contact does not suffice to bring about chemical combination in this case, and even if we were to dissolve the sulphur in bisulphide of carbon, the iron would still remain unacted upon. But if we gently heat the mixture of iron and sulphur, a reaction takes place, and instead of the original substances we have a dark brown mass formed, from which neither can the iron be extracted by a magnet, nor the sulphur be dissolved by bisulphide of carbon.

Chemical combination has taken place between the iron and sulphur in the proportions of the atomic weights of these elements, and sulphide of iron has been formed. The chemical change may be expressed by the equation—

$$Fe + S = FeS.$$

A second type of reaction is that in which a compound substance is decomposed into simpler constituents. To illustrate this we may examine the action of heat on the red oxide of mercury.

Exp. 12.—Heat a small quantity of red oxide of mercury in a test-tube ; it will first darken in colour, and then slowly disappear ; there will be formed a bright metallic mirror on the sides of the tube. The mirror readily yields silver-white liquid globules, answering in all respects to mercury, while in the tube it may be found that the air has been replaced by a gas which supports combustion even more strongly than air. A glowing splinter placed in the tube will burst into a flame.

The gas in the tube is oxygen, and the red powder has been resolved into mercury and oxygen. If we should further determine the weight of the oxide of mercury taken, and that of the mercury left, we should find that the composition of the oxide of mercury, that is, the relation between the amount of mercury and oxygen it contained, is constant.

The third type of chemical change is that which takes place when the substances entering into the reaction are complex, and the reaction consists in a mutual exchange of constituents between the bodies. This is termed *double decomposition.*

Exp. 13.—Place in a test-tube some of the sulphide of iron produced in Exp. 11, and add a little dilute sulphuric acid. A gas is evolved, having an odour of rotten eggs. Soon the evolution of gas ceases, even though some of the sulphide of iron remains. The liquid has changed its character, and is now no longer capable of acting on sulphide of iron. Allow any particles to settle, and when the liquid is quite clear pour it off into a porcelain basin, and evaporate it nearly to dryness ; on cooling, pale green crystals will separate out. By adding more sulphuric acid the whole of the sulphide of iron may be dissolved, and more of the green crystals obtained.

The reacting bodies, sulphide of iron and sulphuric acid, have been transformed into a gaseous body and the green crystals. An examination of the products shows that the hydrogen of the sulphuric acid and the iron of the sulphide of iron have mutually replaced each other, giving rise to the gas (sulphuretted hydrogen SH_2), and the green crystals (sulphate of iron). And if we determine the relative quantities of the substances concerned in the reaction, we shall find that they are such as to be represented by the equation—

$$FeS + H_2SO_4 = \underset{\text{Ferrous Sulphate}}{FeSO_4} + H_2S.$$

Indestructibility of matter.—In the experiments with mercury and iodine, we have seen that though the mercury and iodine have disappeared as such, there has been formed a new body, an iodide of mercury, and by means of the balance we may satisfy ourselves that the weight of the iodide of mercury is *exactly* the same as the combined weight of the mercury and iodine used to produce it.

And so it will be in the case of the sulphide of iron. But in the case of the oxide of mercury in Exp. 12, the proof will be more difficult to carry out. The oxide of mercury and the mercury resulting from its decomposition we may arrange to weigh with an approach to accuracy, but the oxygen which is given off is not so easily dealt with. It must be collected in such a way that there shall be no loss, and when this is done it must be weighed. Both these operations call for considerable experimental ability; when, however, they are successfully performed we find, as in the previous cases, that the total weight of the mercury and oxygen is *exactly* that of the oxide of mercury which has been decomposed.

And whatever chemical changes we submit to the test of the balance, the conclusion is the same : *there is no exception.* We are therefore convinced by such results *that matter may be transformed, but cannot be destroyed.*

The familiar operations of combustion at first sight seem opposed to this statement, but it is merely that the products of combustion are chiefly gaseous, and thus, unless special means are adopted, they escape recognition. We have indeed *solid* fuel reacting with *gaseous* oxygen, with the production of *gaseous* carbon dioxide and water. This will be more fully appreciated when we have considered the nature of combustion.

Transformations of Energy.—Up to this point we have learnt that when chemical action is set up there is a rearrangement of the chemical constituents of the bodies which take part in the reaction. Such a view, however, overlooks altogether the **energy** which is always associated with chemical change. Thus heat is usually evolved or absorbed in a chemical change. Let us therefore make some observations on the heat evolved during chemical combination.

Exp. 14.—Place in a beaker 100 grammes of freshly-burnt lime broken into pieces about the size of a hazel-nut; pour a litre of cold water (noting its temperature) over it, stirring after a few moments, when the lime has fallen to powder, with a glass rod. The lime enters into combination with some of the water and heat is evolved, as may be seen by taking the temperature with a thermometer. A rise of temperature approaching 30° C. will be noted, and this notwithstanding that some of the heat is dissipated by radiation during the experiment. This large amount of heat is due to the combination of the lime with the water to form a new compound, viz. slaked lime, a substance met with in solution in *lime-water*.

But we must not assume that all the heat evolved when substances react upon one another is due to the chemical changes which occur. Frequently, changes of physical condition take place alongside chemical changes, and must be taken account of if we desire to estimate the heat arising from chemical action. The following experiments with sulphuric acid and water will afford a striking example of this.

Exp. 15.—Measure out 50 cubic centimetres of concentrated sulphuric acid and 300 cubic centimetres of water. The temperature[1] of the liquids should be noted. Pour the water into a beaker, and then add the sulphuric acid, and stir them well together with a glass rod. Again note the temperature, and it will be found to have risen about 40° C.

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[1] It is convenient to have both at the same temperature, which may be effected either by cooling them to zero in ice, or by allowing them to stand for some hours in the same room. The former is best for experiment 16—and the latter for experiment 15.

Exp. 16.—Measure out 50 cubic centimetres of concentrated sulphuric acid, and weigh out in a beaker 300 grammes (1 gramme water = 1 cubic centimetre) of snow or finely-powdered ice. Pour the acid into the snow and stir well. The snow will be observed to melt rapidly, and on taking the temperature of the mixture it will be found that instead of the considerable rise of temperature which occurred in the previous experiment, we have a lowering of temperature approaching eighteen degrees Centigrade; that is to say, with sulphuric acid previously cooled to zero the final temperature will approach − 18° C. An excellent freezing mixture may indeed be made by mixing sulphuric acid and snow.

Now how are we to account for the great difference between the results of these two experiments? The sulphuric acid in the latter experiment combines with the water, and the heat evolved in consequence of the combination is just as great as it was in the former.

On comparing the experiments, the only difference we note is that in one case liquid water is used and in the other, solid water (snow), and the heat absorbed in the fusion of the snow must be held accountable for the variation of 58° C. between the two records.

Again, when a gramme of hydrogen is burnt in oxygen, the heat arising from the combustion is sufficient to raise the temperature of a litre of water a little more than 34° C. About five-sixths of this heat is due to the transformation of chemical energy, in the process of combination, into heat, the remainder coming from the condensation of the steam formed during the combustion.

Water may be decomposed again into its elements by means of a current of electricity, and affords an interesting example of the transformation of energy. In the course of the decomposition electrical energy is being transformed into chemical energy. If we inquire into the source of the electrical energy, we shall find that it is generated by dissolving the zinc of the cells of the battery in sulphuric acid—a transformation of chemical energy into electrical energy.

So that here we have an instance of the transformation of chemical into electrical energy, which is transformed again into chemical energy when the water is decomposed. Or again, if we connect up the poles of the battery by means of a *thin* platinum wire, this will become heated, the electrical energy being transformed into heat during its passage along the wire.

Conservation of energy.—Just as the balance has proved that there is no destruction of matter, so a measurement of the energy concerned in various operations has shown that it is impossible to destroy energy. "The total energy of any body or system of bodies is a quantity which can neither be increased nor diminished by any mutual action of these bodies, though it may be transformed into any of the forms of which energy is susceptible." Energy may be defined as the capacity for doing work. Steam has a greater capacity for doing work than water, and when steam is converted into water there is apparently a loss of energy, but really only a transformation of part of the energy into the heat which accompanies the condensation of steam to water.

Chemical attraction.—Such transformations of energy take place in every chemical reaction. The intrinsic energy of hydrogen and oxygen in the free state is greater than that of the water vapour to which they give rise, by the amount of energy (chemical attraction) exerted between hydrogen and oxygen in the process of combination; thus heat is evolved. Freshly-burnt lime when moistened with water becomes hot, and the heat is due to the transformation of the energy of chemical attraction exerted between the lime and water. Similar transformations, which are quite manifest, accompany the burning of iron in oxygen, the combustion of coal, etc. Chemical changes are in general accompanied by an evolution of heat, and the same change gives rise (other conditions being the same) to the same amount of heat. It is generally true that the greater the amount of heat generated, the greater is the attraction between the bodies, and the greater the stability of the resulting compound. And it might be thought that the heat evolved is an accurate measure of the chemical attraction exerted; we must, however, bear in mind that every chemical change is accompanied by changes of physical condition, which are also accountable for part of the heat evolved during chemical reaction. In the large majority of cases it may be accepted that the heat evolved when two substances combine with one another is in some degree a measure of the chemical attraction or *affinity* exerted between them, but an accurate estimate of chemical attraction cannot be obtained till the heat arising from changes of physical condition is measured and allowed for.

Law of Definite and Multiple Proportions.

We must now call attention to one other point of great importance, *the proportions in which elements combine together.* We have noticed that in the case of the green iodide of mercury, the sulphide of iron, or the oxide of mercury, the proportions in which the mercury and iodine or the iron and sulphur or the mercury and oxygen unite are expressed by numbers which are definite and invariable. If w be the weight of iodine taken, 1·58 w will always be the weight of the mercury which combines with it to form the green iodide of mercury; so if w^1 be the weight of the sulphur in iron sulphide, 1·75 w^1 will be the weight of the iron; and *whatever chemical compound is examined, the relative proportions of its constituents are fixed and invariable.* This is the law of **definite proportions.**

In addition to this, we notice that the amount of iodine required to form the red iodide of mercury is exactly *twice* that required to convert the same amount of mercury into the green iodide, a fact which finds expression shortly in the formulæ for the two iodides, viz. HgI, HgI_2. We have found

1·58 grms. of Hg combine with 1 grm. of I to form mercurous iodide.
1·58 ,, ,, ,, ,, 2 ,, ,, ,, mercuric iodide.

Relative proportion of iodine combining with the same weight of mercury is 1 : 2.

So 12 grms. of C combine with 16 grms. of O to form carbon monoxide.
12 ,, ,, ,, ,, 32 ,, ,, ,, carbon dioxide.

Relative proportion of oxygen combining with the same weight of carbon is 1 : 2.

32 grms. of sulphur combine with 32 grms. of O to form sulphur dioxide.
32 ,, ,, ,, ,, 48 ,, ,, ,, sulphur trioxide.

Relative proportion of oxygen combining with the same weight of sulphur is 2 : 3.

14 grms. of nitrogen combine with 8 grms. of O to form nitrous oxide.
14 ,, ,, ,, ,, 16 ,, ,, ,, nitric oxide.
14 ,, ,, ,, ,, 24 ,, ,, ,, nitrogen trioxide.
14 ,, ,, ,, ,, 32 ,, ,, ,, nitrogen peroxide.
14 ,, ,, ,, ,, 40 ,, ,, ,, nitrogen pentoxide.

Relative proportion of oxygen combining with the same weight of nitrogen is 1 : 2 : 3 : 4 : 5.

These and all other cases may be summed up in the following statement, which is known as the law of **multiple proportions.** *When one element combines with another in more than one proportion, these proportions bear a ratio to one another which may be expressed by small whole numbers.*

If we mix together two liquids like water and sulphuric acid, or two solids such as carbon and sulphur, we may do this in any proportion whatever, and the differences between the relative proportions of the two constituents may be made as small as we please. The number of mixtures that may be made from the two liquids or the solids, each differing from the other in composition, may be indefinitely large.

But if now we seek to *combine* two substances together, we shall find a marked difference; 12 parts by weight of carbon may combine with 32 parts by weight of sulphur and no less than this. If more sulphur than this can be induced to *combine*, the amount will not be indefinitely small or large, as was the case with the mixing operation; it will be again 32 parts more by weight, that is 12 parts by weight of carbon to 64 parts by weight of sulphur. The amount of sulphur which enters into combination with the same weight of carbon increases not gradually but *by steps*, each step implying the addition of 32 parts of sulphur per 12 parts of carbon.

And if we examine the whole series of chemical compounds which contain sulphur we shall find that combination is invariably a *step by step* process.

The smallest relative mass of each element which enters into combination, (*e.g.* H = 1, C = 12, O = 16, S = 32, etc.), is called the *combining weight.*

By the application of the balance it is possible to demonstrate that the constituents of a given compound are present in definite proportions, and in a number of instances this may be done very simply.

Exp. 17.—Weigh a small test-tube, introduce about a gramme of powdered potassium chlorate and weigh again; the increase will of course represent the weight of potassium chlorate taken. Now heat in the Bunsen flame; the substance first melts and gives off a gas (oxygen, see p. 92); it then thickens, gives off more gas very rapidly, and ultimately, after the heating has been continued some minutes, no further change is observed. There is left in the tube while hot a molten colourless residue which solidifies to a white mass on cooling. When fully cold weigh the tube again.

By deducting the weight of the tube in the last we have the weight of the residue (potassium chloride, see p. 92). All samples of potassium chlorate however prepared will yield the same proportion of residue, viz. very nearly 0·6 grm. per gramme of the chlorate taken.

Mercuric oxide, carbonate of magnesia or of lime, silver oxide and many other substances may be experimented on in a similar manner.

Or the principle may be illustrated synthetically by burning certain known weights of some of the elements in air, by which they will be found to undergo an increase in weight (see p. 6). In all these cases the change of weight associated with a definite change of composition is itself always found to be perfectly definite.

SUMMARY.

1. For bodies to react upon one another—
   (*a*) there must be intimate contact between them;
   (*b*) mere contact of solids is not usually sufficient; more intimate contact is effected and the conditions are more favourable to chemical change when the substances are in solution or in state of vapour. Hence heat facilitates chemical change.

2. Chemical reactions may be classified thus:—
    (*a*) direct combination between two or more bodies;
    (*b*) direct decomposition into two or more bodies;
    (*c*) double decomposition, where both the reacting bodies effect a mutual exchange of constituents.
3. Experience shows that chemical change consists merely in a *transfer* of matter, and if suitable means are taken proof can always be afforded that there is no loss or destruction of matter.
4. Similarly, during chemical change, energy may be transformed, but is not destroyed.
5. When elements combine together they do so *in definite proportions.* When they do so in more than one proportion, and with a given mass m of elements A there combine masses p q r . . . of element B, then $p:q:r$, etc., will always be found in the ratio of small whole numbers, such as 1 : 2 : 3, etc., or 2 : 3, or 3 : 4, or 2 : 5. This is known as the law of *multiple proportions.*

QUESTIONS.—CHAPTER II.

1. How would you convert the green iodide of mercury into the red iodide?
2. How would you ascertain whether a sample of red iodide of mercury contained any free iodine?
3. You are given (*a*) a compound of mercury and iodine, (*b*) a mixture of mercury and iodine containing precisely the same amount of each of these elements as the compound; what differences would be observable between the two?
4. State the phenomena which are usually to be observed whilst chemical combination is taking place.
5. In what respects does chemical attraction differ from gravitation and from magnetism?
6. Two elements (solids) are brought into contact, but without undergoing combination; what means would you employ in order to induce them to combine?
7. Why is a substance usually more ready to take part in chemical reaction when it is in the form of vapour rather than in the solid condition?
8. Explain in words the precise meaning of the expression—

$$Fe + S = FeS.$$

9. What is meant by *combination*, *decomposition*, *double decomposition?* Give examples of each.
10. What is the nature of the evidence which leads us to conclude that matter is indestructible?
11. What is the nature of the evidence which leads us to conclude that energy is indestructible?
12. Give an instance of the transformation of (*a*) chemical energy into heat, (*b*) electrical energy into heat, (*c*) electrical energy into chemical energy.
13. What changes other than chemical may give rise to the evolution of heat?
14. Explain what is meant by the Conservation of Energy.
15. State the law of definite proportions and illustrate it by reference to examples.
16. State the law of multiple proportions, and illustrate it by reference to examples.

CHAPTER III.

HYDROGEN.

HYDROGEN. *Occurrence.*—Hydrogen occurs in the free state as an incandescent gas in the sun, but in the earth it is always found in combination with other elements. Water is a compound of hydrogen and oxygen, H_2O; many oils consist of hydrogen and carbon, and these elements, together with oxygen, form the chief constituents of animal and vegetable tissue, and of organic compounds in general. Hydrogen is usually prepared by the decomposition of water, or of compounds into which water enters as a constituent.

Direct decomposition of water.—This may be effected either at a high temperature, or by means of a current of electricity. By passing steam through a porcelain tube heated to at least 1000° C., Grove was able to show that a part of it underwent decomposition into hydrogen and oxygen.

But by means of the following arrangement water may be decomposed into the elements hydrogen and oxygen, and these gases may be collected in the proportions in which they exist in water.

> **Exp. 18.**—The apparatus shown in Fig. 2 is of glass except the wires bearing strips of foil fused into each limb of the U-tube near the bend: these are of platinum, and are called the electrodes. The apparatus is filled up to the bulb with water containing a little sulphuric acid,[1] and each electrode is connected

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[1] Water is practically a non-conductor of electricity, and a little sulphuric acid must be added to it to enable the electric current to pass; indeed we may regard the decomposition as being that of dilute sulphuric acid.

by a copper wire with a pole of a battery of four Bunsen's or Groves's cells. As soon as the connection is made, gas is seen to rise from the electrodes, and to collect in the tubes. The volume of gas collected in one tube will be observed to be twice as great (or rather more, owing to the greater solubility of oxygen in water) as that in the other, and on examination it will be found that this gas is inflammable, and shows the properties of hydrogen, whilst the other will prove to be oxygen.

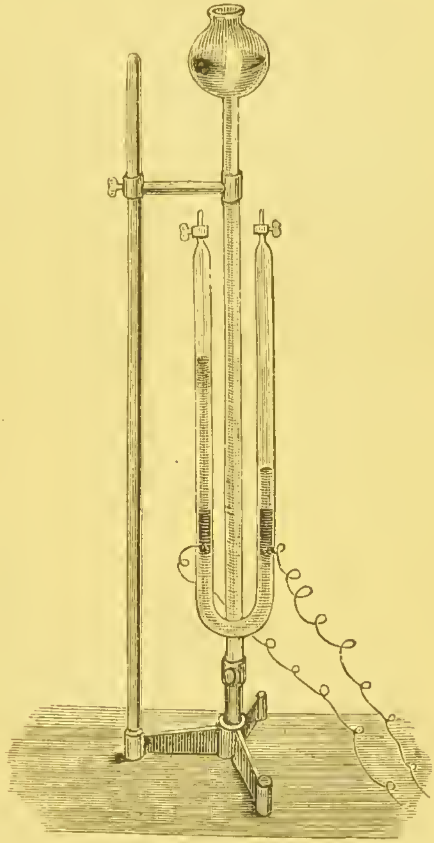

Fig. 2.

Decomposition of water by the action of certain elements.—The alkali metals (K, Na, Li, etc.), and also those of the alkaline earths (Ba, Sr, Ca), decompose water at ordinary temperatures. Only half the hydrogen of the water is liberated in this case, the reaction being represented by the following equation—

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2.$$

Caustic soda ($NaOH$) is formed and dissolves in the water, imparting to it a soapy feeling, and rendering it alkaline, as may be shown by pouring red litmus into the liquid.

Iron, zinc, magnesium, and even carbon, *at moderately high temperatures*, decompose water. Thus, by passing steam over red-hot iron, the oxygen of the steam combines with the iron, and hydrogen is set free, and may be collected as in Exp. 20.

$$3\,Fe + 4\,H_2O = \underset{\text{Magnetic oxide of iron.}}{Fe_3O_4} + 4\,H_2.$$

Steam passed over red-hot coke forms what is known as **water-gas**, which contains a large proportion of hydrogen; oxygen compounds of carbon are formed, however, at the same time, and, being gaseous, pass over with the hydrogen. This method would therefore not be suitable for obtaining pure hydrogen.

Fluorine decomposes water at ordinary temperatures with great readiness, and chlorine does so in presence of sunlight.

$$2\,F_2 + 2\,H_2O = 4\,HF + O_2 \text{ (ozone is formed here).}$$
$$2\,Cl_2 + 2\,H_2O = 4\,HCl + O_2.$$

Exp. 19.—Small pieces of sodium the size of a pea are thrown upon the surface of distilled water. Hydrogen is given off, and if each piece of metal is held under the mouth of a cylinder of water, by using a gauze net as shown in the diagram, the gas may be collected and examined.

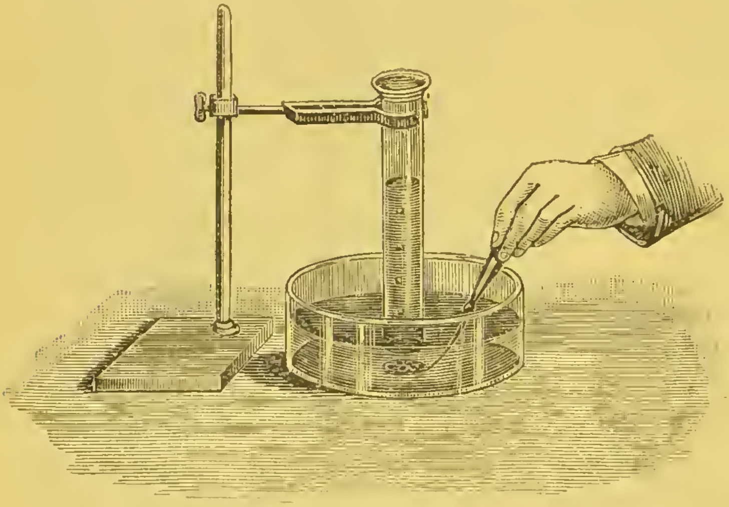

FIG. 3.

We learn therefore that water may be decomposed (1) by heat; (2) by a current of electricity; (3) by some elements which possess a great affinity for oxygen—liberating hydrogen; and others which possess a great affinity for hydrogen—liberating oxygen: for example, sodium and chlorine respectively.

Action of metals on dilute acids as a means of preparing hydrogen.—When hydrogen is required in quantity and of a moderate degree of purity, it is best prepared in this way, zinc and dilute sulphuric acid being convenient re-agents for the purpose; some other metals, such as iron or magnesium, may however be employed, and hydrochloric acid may be substituted for sulphuric acid. Indeed, *as a general rule*, acids, when acted upon by metals, liberate hydrogen as the primary product.

Exp. 20.—Introduce into a twelve-ounce flask, fitted with safety funnel and delivery-tube as shown in the figure, 10 grammes of zinc, and add 180 c.c. of dilute sulphuric acid.[1] Bubbles of gas will be observed to rise at the zinc, and the gas passing out of the delivery-tube may be collected in strong glass cylinders as shown.

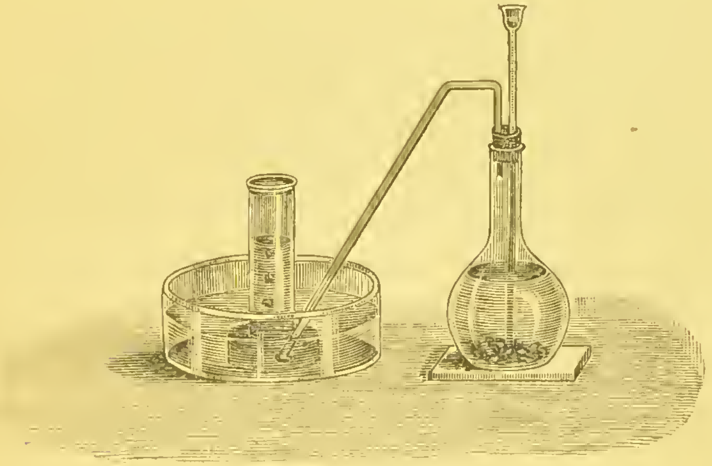

FIG. 4.

Some cylinders of the gas may be obtained and reserved for an experimental investigation of the properties of hydrogen. When the action has ceased, the clear liquid from the flask may be poured into a porcelain basin, and evaporated until it has been reduced to about 20 c.c. in bulk. On allowing this liquid to cool, crystals of a white salt will be observed to separate out; the zinc has displaced the hydrogen of the sulphuric acid and formed sulphate of zinc.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

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[1] Prepared by previously mixing the concentrated acid with eight times its volume of water.

Properties of hydrogen.

Exp. 21.—Take the cylinder of gas first collected, and holding it mouth downwards, apply a light—the hydrogen will burn instantaneously throughout the vessel with explosion, owing to its being intimately mixed with air carried over from the flask in which the hydrogen was generated. The second cylinder, treated in the same way, will probably be found to burn quietly, as it contains very little air. Notice that the hydrogen only burns in this instance where it has access to air, namely, at the mouth of the cylinder; also that a lighted taper pushed up into the cylinder whilst the hydrogen is burning will be extinguished. We see, therefore, that hydrogen burns where it comes into contact with the air, but will not support the combustion of a taper.

Exp. 22.—Take a *dry* cylinder, somewhat smaller than those used for collecting the gas, and holding it mouth downwards transfer the hydrogen from one of the cylinders into it by pouring upwards. The hydrogen will rise in the dry cylinder and displace the air from it. Now apply a light to the mouth of this cylinder and there will be a slight explosion, owing to a small admixture of air during the transference, whilst the gas will burn and moisture appear on the sides of the cylinder. (Also see Exp. 45.)

We learn from this experiment that hydrogen is lighter than air, and that when it burns water is formed. The burning consists in the combination of hydrogen with the oxygen of the air.

As by heat or electricity we are able to decompose water, and ascertain by an *analytical* method that it is composed of hydrogen and oxygen, so in this experiment we have *synthesized* water from the elements hydrogen and oxygen.

SUMMARY.

1. Hydrogen occurs in the free state in the sun and stars.
   ,, ,, in combination with oxygen in water and some mineral substances; also in animal and vegetable organisms, associated with carbon, oxygen, etc.

2. *Hydrogen preparation :—*
    - (*a*) Electrolysis of water or dilute acids ;
    - (*b*) Decomposition of water or dilute acids by metals.
3. *Properties :—*
    - (*a*) Lightness ;
    - (*b*) Combustibility ;
    - (*c*) Non-supporter of combustion ;
    - (*d*) Combines directly with oxygen to form water.

QUESTIONS.—CHAPTER III.

1. Name some natural substances which contain hydrogen as an essential constituent. Is hydrogen known to occur in the free state?
2. How may water be decomposed without the application of chemical re-agents?
3. Name elements which decompose water—
   (*a*) at ordinary temperature with the liberation of hydrogen;
   (*b*) at ordinary temperature with the liberation of oxygen;
   (*c*) at red heat.
   Give equations showing the nature of the reaction in each case.
4. If you desire to obtain hydrogen in as pure a condition as possible, what method would you adopt?
5. If you desire to prepare moderately pure hydrogen in large quantities, what method would you adopt?
6. Write down equations showing the action of iron and magnesium respectively on dilute sulphuric acid.
7. Devise three experiments suitable for illustrating in a striking manner the extreme lightness of hydrogen.
8. What chemical change takes place during the burning of hydrogen in air?
9. How would you show that moisture results from the combustion of hydrogen? Ordinary coal gas when burnt also gives rise to the formation of moisture; what conclusion would this lead you to draw as to the composition of coal gas?
10. A light is brought to the mouth of an inverted cylinder of hydrogen; it is noticed that flame at first appears round the mouth of the cylinder but none inside, afterwards the flame gradually rises within the cylinder: explain these phenomena.

CHAPTER IV.

CHLORINE.

A COMPARISON of the physical and chemical properties of the four elements, fluorine, chlorine, bromine, and iodine, termed the halogens, and of their compounds, readily lead one to regard these elements as forming a natural group.

And this not so much from the closeness of the resemblance as from the fact that there is a gradual transition in properties which proceeds always in the same order, viz. in the order of their atomic weights. A general survey of the group will illustrate this.

Physical properties of these elements.—Fluorine is a gas which does not condense to a liquid even when cooled down to − 95° C.; it possesses a very faint greenish-yellow colour ; chlorine is much more readily condensible, and has a distinct greenish colour; bromine is at ordinary temperatures a reddish-brown liquid boiling at 59° C. and solidifying at − 7° C., whilst iodine is a black crystalline solid which boils at 184° C., its vapour being of a beautiful violet colour.

In the gaseous condition these elements have a very irritant action on the mucous membrane which is most marked in the case of fluorine and chlorine, and least so with iodine. They have an odour resembling that of seaweed if they are in a largely diluted condition.

Their solubility in water follows the order of their atomic weight; chlorine, the most soluble (fluorine decomposes water), dissolving in about half its volume of water, bromine to the extent of three parts in 100 of water, whilst iodine is only very slightly soluble in water, but dissolves readily in alcohol, ether, bisulphide of carbon, or in a solution of potassium iodide.

When chlorine is passed into water to saturation at 0° C., yellow crystals having the composition $Cl_2 . 8\ H_2O$ separate out. On warming these crystals they readily decompose with the evolution of chlorine. Bromine under similar circumstances forms crystals having the composition $Br_2 . 10\ H_2O$.

General Chemical Properties.—Whilst the tendency to combine with oxygen *increases* as we pass from fluorine to iodine, the affinity for hydrogen and the metals *decreases.* Fluorine forms no compound with oxygen, chlorine can only be made to combine indirectly and forms unstable oxides, iodine however is directly oxidized by nitric acid, and its oxide is much more stable. Hydrogen, on the other hand, combines directly even *in the dark* with fluorine and at very low temperatures, but with chlorine the combination only takes place on heating or under the stimulus of rays of light of great chemical activity, and bromine and iodine are induced to combine with hydrogen with much greater difficulty.

Moreover, the stability of the products of such action, HF, HCl, HBr, HI, shows a falling off in the order named.

The interaction of the halogens and water is instructive. Fluorine decomposes water immediately at ordinary temperatures, and with considerable energy, giving rise to the formation of ozone. Chlorine acts readily and bromine feebly at ordinary temperatures, but only in sunlight; iodine is without action.

Chlorine-Occurrence.—Chlorine is not found in the free state in nature, but occurs in combination in rock-salt ($NaCl$). Sylvine (KCl), and Carnallite ($KCl . Mg\ Cl_2 . 6\ H_2O$). Free hydrochloric acid and ferric chloride (Fe_2Cl_6) have also been observed in volcanic regions. The chlorides being fully soluble are found in large quantity in sea-water (see p. 85).

Preparation of Chlorine.—Sodium chloride (and most other chlorides) may be used as the source of chlorine. When treated with manganese dioxide and sulphuric acid the following reaction takes place—

$$2\ NaCl + 3\ H_2SO_4 + MnO_2 = 2\ NaHSO_4 + MnSO_4 + 2\ H_2O + Cl_2.$$

More usually in preparing chlorine, concentrated hydrochloric acid is substituted for the common salt and sulphuric acid, the reaction being—

$$4\ HCl + MnO_2 = MnCl_2 + 2\ H_2O + Cl_2.$$

The reaction may be performed in a flask fitted with a safety funnel similar to that used in preparing hydrochloric acid; very gentle heat is required.

The gas should be passed through a wash-bottle containing concentrated sulphuric acid especially where it is of importance that it should be dry, as in experiment 29.

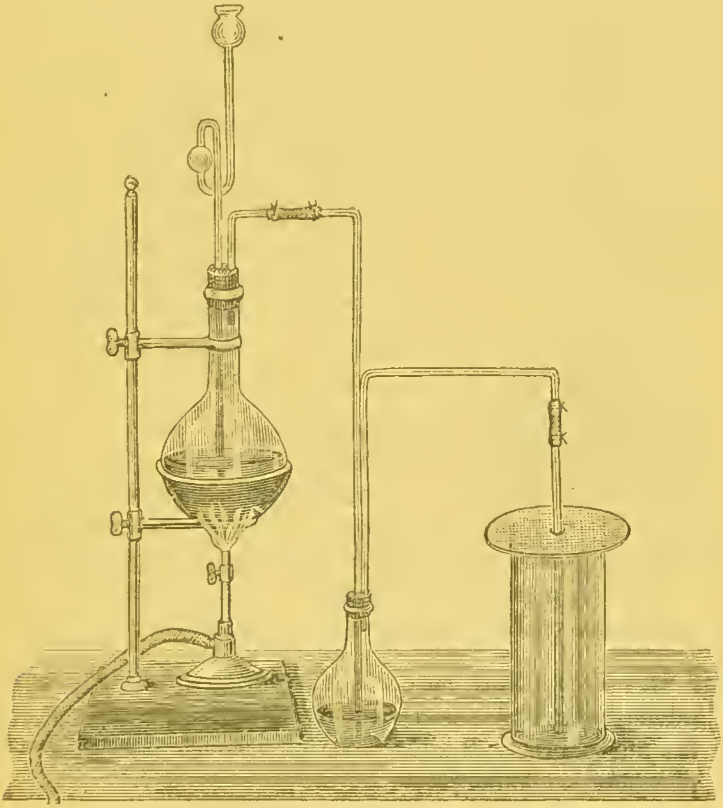

FIG. 5.

Exp. 23.—Pass chlorine for some minutes through about 50 c.c. of water, and to about 20 c.c. of this add a solution of sulphuretted hydrogen; hydrochloric acid is formed, the liquid becoming turbid owing to the separation of sulphur, according to the equation—

$$Cl_2 + H_2S = 2\ HCl + S.$$

Exp. 24.—Fill a Cowper's tube with chlorine water (see figure), and expose to direct sunlight; bubbles of gas will be seen to rise in the liquid. When sufficient gas has collected it may be tested with a glowing splinter, and will be found to be oxygen. The change which has taken place is represented by the equation—

$$2\ Cl_2 + 2\ H_2O = 4\ HCl + O_2.$$

Chlorine is soluble in water and acts upon mercury, it is therefore collected by downward displacement, and six jars of it may be obtained in this way, using precautions to avoid inhaling the gas.

Exp. 25.—Introduce a lighted jet of hydrogen into a jar of chlorine. It continues to burn with the production of fumes of hydrochloric acid, which may be made more visible by bringing a drop of ammonia liquor to the mouth of the jar.

Exp. 26.—In the same manner burn coal gas in chlorine; it will be seen that the flame becomes duller and more smoky. Hydrochloric acid is produced as in the previous experiment from the hydrogen in the coal gas, and the smokiness of the flame is due to the separation from the coal gas of carbon with which the chlorine does not unite.

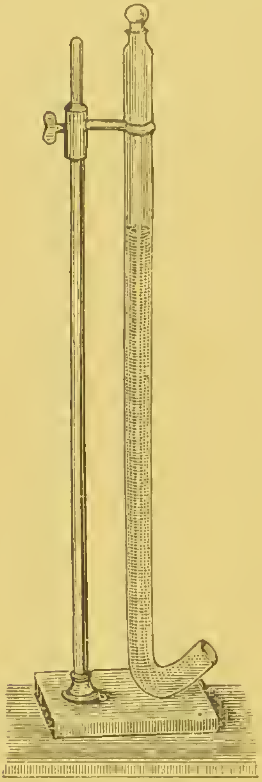

Fig. 6.

Exp. 27.—Into a third jar of chlorine bring a piece of phosphorus on a deflagrating spoon and without the application of heat; presently the phosphorus will ignite and burn feebly with the formation of phosphorus trichloride—

$$2\ P + 3\ Cl_2 = 2\ PCl_3.$$

Antimony, copper and some other metals in a finely divided condition also ignite when plunged into chlorine.

Exp. 28.—Heat a piece of sodium in a deflagrating spoon until it takes fire, and then plunge it into a jar of chlorine; the sodium burns brilliantly, uniting with the chlorine to form sodium chloride.

The bleaching of vegetable colouring matters.—Chlorine possesses the property of depriving the leaves of plants, flowers and vegetable dyes of their colour. In the absence of moisture no such action however takes place, the bleaching being due to the oxidation of the colouring matter by *nascent* oxygen resulting from the interaction of chlorine and water (see Exp. 24). Certain oxidizing agents which likewise furnish nascent oxygen, notably hydrogen peroxide, have a similar action.

Exp. 29.—Place a piece of dry cloth dyed with turkey-red in a stoppered jar of dry chlorine, and leave it some minutes; no decolourization will occur, but on moistening the cloth it will be bleached.

Exp. 30.—Place a printed label, smeared with writing ink, in a jar of moist chlorine; in a little while the ink stains will disappear whilst the printing ink will be unaffected.

The basis of the writing ink is a vegetable colouring matter which is acted upon by the chlorine, but the printer's ink consists essentially of carbon, which, as we have seen in experiment 26, is not acted upon by chlorine.

SUMMARY.

1. The elements F, Cl, Br, I afford an excellent example of a chemical family.

   Physical properties show a gradation from the gaseous fluorine, uncondensed at − 95° C., to iodine, solid at ordinary temperatures and even up to 184° C.

   Specific gravity, atomic weight, and other physical properties follow in a similar order.

   Chemical properties.

   Note that in the order of increasing atomic weight, viz. in the order F, Cl, Br, I.

   (*a*) affinity for oxygen increases;
   (*b*) „ „ hydrogen decreases.

Chlorine.

2. *Preparation.*—

   (*a*) By electrolysis of HCl.

(*b*) By the action of H_2SO_4 and manganese dioxide on chlorides, or by action of manganese dioxide on HCl.

3. *Properties.*—
    (*a*) Solubility in water—the crystalline hydrate;
    (*b*) Action of H_2S on a solution of chlorine;
    (*c*) Action of sunlight on a solution of chlorine;
    (*d*) Combustion of hydrogen (or coal gas) in chlorine;
    (*e*) " " P, Sb, Cu and Na " "
    (*f*) Bleaching of vegetable colouring matters.

QUESTIONS.—CHAPTER VII.

1. Draw up in tabular form a comparison between the halogen elements with regard to (*a*) their colour, (*b*) their solubility in water, (*c*) their action on water, (*d*) their affinity for hydrogen.
2. How may chlorine be obtained in the free state (*a*) from hydrochloric acid; (*b*) from potassium chloride?
3. What is the action of sulphuretted hydrogen on chlorine water?
4. Describe what takes place when a solution of chlorine in water is exposed to sunlight.
5. Describe the chemical changes which accompany the burning of a candle in chlorine, and show how far they account for the peculiar appearance of the flame which is observed when a candle burns in chlorine.
6. Give instances of other elements besides hydrogen which readily combine with chlorine.
7. Chlorine has been described as a body of great chemical activity; what observations with regard to its behaviour lend support to such a view?
8. Explain the chemical change which takes place during the process of bleaching.
9. Why is printer's ink permanent in presence of chlorine?

CHAPTER V

HYDROCHLORIC ACID.

Preparation of hydrochloric acid gas.

Hydrogen combines directly with chlorine—

(*a*) when a jet of hydrogen burns in chlorine ;

(*b*) when a mixture of hydrogen and chlorine is placed in a closed vessel and ignited by passing a spark ;

(*c*) when a mixture of these gases is exposed to sunlight or the flash of burning magnesium, the combination taking place instantaneously with explosion ;

(*d*) when a mixture of the gases is exposed to diffused daylight, the combination taking place slowly and without explosion.

Hydrochloric acid gas is most conveniently prepared by the action of concentrated sulphuric acid on common salt (sodium chloride)[1] ; on *gently* heating the mixture the following reaction takes place—

$$\underset{\text{Sodium chloride.}}{NaCl} \quad + \quad H_2SO_4 \quad = \quad \underset{\text{Sodium hydrogen sulphate.}}{NaHSO_4} \quad + \quad HCl.$$

and when a higher temperature is employed the sodium hydrogen sulphate reacts further—

$$NaCl \quad + \quad NaHSO_4 \quad = \quad \underset{\text{Sodium sulphate.}}{Na_2SO_4} \quad + \quad HCl.$$

The two stages of this reaction may be summed up together thus, regarding only the ultimate products—

$$2\ NaCl + H_2SO_4 = Na_2SO_4 + 2\ HCl.$$

[1] All chlorides, except those of silver and mercury, yield hydrochloric acid when treated with sulphuric acid.

The preparation is carried out in a flask fitted with safety funnel and delivery-tube, as shown in the figure. In consequence of the great solubility of the gas in water, it must be collected over mercury or in dry cylinders by displacement of air.

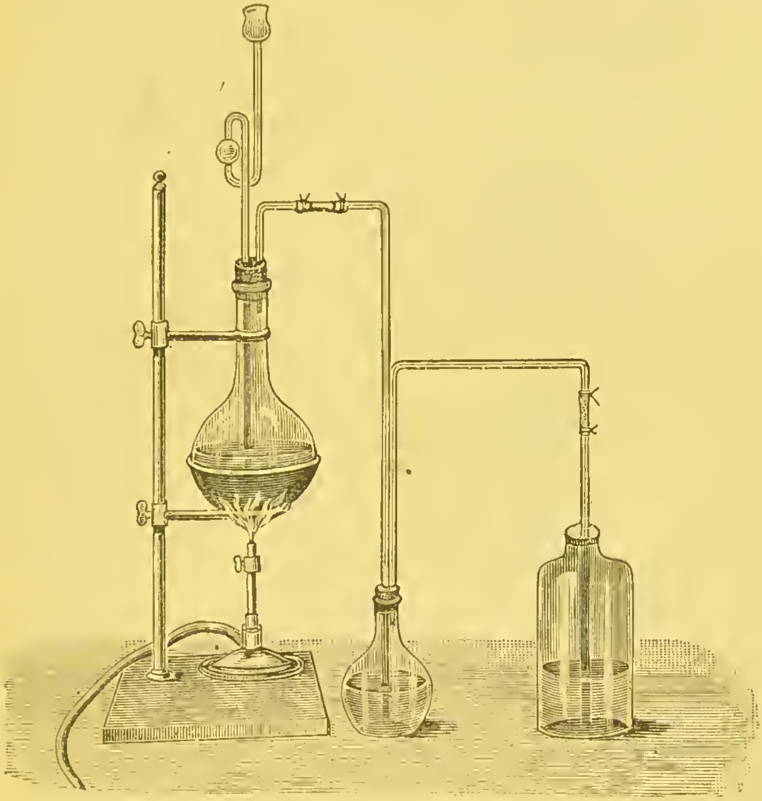

FIG. 7.

Properties of the gas.

Exp. 31.—Pass the gas rapidly through a few cubic centimetres of water; it will be found to dissolve very freely in the water, yielding a strongly acid solution. The concentrated hydrochloric acid used as a reagent is a saturated solution prepared in this way, and contains about 40 to 45 per cent. by weight of hydrochloric acid. This experiment shows the *very great solubility* of hydrochloric acid gas in water. This may also be effectively exhibited by the following device.

Exp. 32.—Fill a large bolt-head, of at least two or three litres content, with hydrochloric acid gas by displacement. Fit it with an india-rubber cork, through which passes a tube with stop-cock, and drawn out into a jet as shown. Dip the extreme end of the tube into water and open the stop-cock.

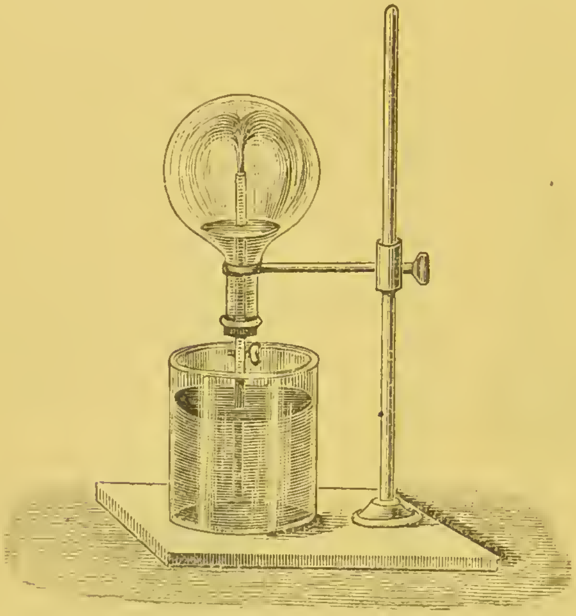

FIG. 8.

Under these conditions the gas at first only comes into contact with the water very slowly by a process of diffusion, and it is desirable to bring about contact with a larger surface of water by cooling the flask; this may be done by pouring a few drops of ether over its surface. When the jet once comes into play the water continues to rise into the flask until all the hydrochloric acid is absorbed.

Water at 0° C. absorbs 503 times its volume of the gas.

Hydrochloric acid is a colourless gas which fumes in moist air, and has a strongly irritant action on the mucous membrane. A weak aqueous solution of the gas when boiled under normal pressure becomes stronger, until it contains 20·24 per cent. of the gas, and a stronger solution than this, when boiled, grows weaker, and ultimately falls to 20·24 per cent. strength. A solution of this strength distils unchanged at 110° and 760 m.m.

Dry hydrochloric acid gas may be condensed under a pressure of 40 atmospheres at zero, forming a colourless liquid. It is a remarkable fact that whilst the aqueous solution of the gas readily acts upon metals, oxides, carbonates, etc., the anhydrous gas and the liquefied acid are much less active. Liquefied hydrochloric acid has been shown to be entirely without action upon iron, zinc, magnesium, and many other metals, and will not even decompose anhydrous carbonates.

The chlorides.—We have seen that hydrogen in combination with chlorine forms an acid. Many of the elements, when brought into this acid, replace the hydrogen and form a *salt*, the acid character either disappearing altogether, or becoming much less pronounced. If the oxide be employed instead of the metal, there is no hydrogen given off, the salt is formed as before, but the hydrogen combines with the oxygen of the oxide and forms water. Such salts may also be produced in many cases by direct combination of an element with chlorine.

Other methods of preparation of the chlorides will be indicated in the following experiments—

Exp. 33.—Dilute hydrochloric acid with five times its volume of water, and to 20 cubic centimetres of this add metallic magnesium little by little so long as any effervescence occurs, and until some of the magnesium remains in excess. Now decant the clear liquid into a porcelain basin, and evaporate nearly to dryness over a water-bath. A crystalline substance will separate out on cooling; this is the chloride of magnesium ($MgCl_2 . 6 H_2O$), the gas which was evolved during the solution of the magnesium being hydrogen.

$$Mg + 2 HCl = MgCl_2 + H_2.$$

Dry the salt on filter paper and then dissolve it in water, and add a few drops of litmus solution; it will be found to be neutral, or if the mother liquor has not been completely removed, faintly acid.

Exp. 34.—To 20 cubic centimetres of the dilute hydrochloric acid add barium carbonate in excess. Decant off the clear liquid and evaporate to small bulk as before, crystals of barium chloride ($BaCl_2$ 2 H_2O) will separate out. The gas which is evolved in this case is carbon dioxide.

$$BaCO_3 + 2 HCl = BaCl_2 + CO_2 + H_2O.$$

Barium chloride, like magnesium chloride, dissolves in water, forming a neutral solution.

Exp. 35.—To 20 cubic centimetres of hydrochloric acid add a few drops of litmus solution, and then add gradually a solution of caustic potash until the bright red colour of the litmus changes to port-wine red (if too much potash is added it will become blue). Now evaporate as before, and crystals of potassium chloride will separate out—

$$\underset{\text{Caustic potash.}}{KHO} + HCl = KCl + H_2O.$$

There will be no evolution of gas in this case, unless the potash should contain some carbonate as an impurity.

Exp. 36.—To a solution of nitrate of lead add hydrochloric acid: a white precipitate is formed consisting of chloride of lead. In this case the chloride which is formed is only slightly soluble in the cold, and it separates out without evaporation. Decant off the clear liquid and boil some of the salt with water. If sufficient water is added it will dissolve completely and separate out again in crystals on allowing the solution to cool slowly, the chloride of lead being soluble in 20 parts of hot water and in 135 parts of cold water.

Summing up, we have as methods for the preparation of the chlorides—

(1) Direct combination of elements with chlorine.

(2) Solution of the metal, the oxide, hydrate, or carbonate in hydrochloric acid.

(3) The addition of hydrochloric acid or a soluble chloride to a solution of a salt of the metal with the production of an insoluble, or slightly soluble, chloride.

The nature of acids and salts.—In the same sense that we regard the chlorides as compounds of chlorine with the metals, we may look upon hydrochloric acid as a compound of chlorine with hydrogen. All **acids** contain hydrogen, and may be regarded as hydrogen salts in which the hydrogen is replaceable by metals to form what are ordinarily termed "salts"; acids are usually sour to the taste and often corrosive. They all possess the property of turning a solution of the vegetable colouring matter, litmus, red, and a body which exhibits this property is said to have *an acid reaction* to litmus.

Tests for the hydrochloric acid and its salts.

1. A solution of silver nitrate, $AgNO_3$, when added to a solution of hydrochloric acid or a chloride gives a white curdy pre-

cipitate of silver chloride AgCl, soluble in ammonia, insoluble in nitric acid.

2. Free HCl, heated with manganese dioxide, or chlorides heated with manganese dioxide and sulphuric acid, evolve chlorine, which may be easily recognized by its colour, smell, and bleaching action.

SUMMARY.

1. *Hydrogen chloride—preparation—*
    (*a*) by direct union of H and Cl;
    (*b*) by action of sulphuric acid on chlorides.
2. *Properties—*
    (*a*) heavier than air;
    (*b*) great solubility in water;
    (*c*) irritant and corrosive action;
    (*d*) liquefied by pressure;
    (*e*) anhydrous or gaseous liquid HCl much more inert.
3. *The chlorides—*
    (*a*) Moist hydrochloric acid gas or a solution of the gas acts on metals, oxides, carbonates forming chlorides.
    (*b*) Tests for chlorides.

QUESTIONS.—CHAPTER V.

1. Under what circumstances does hydrogen combine directly with chlorine?
2. What is the action of sulphuric acid on sodium chloride (*a*) at ordinary temperatures, (*b*) at a red heat?
3. How would you prepare a saturated solution of hydrochloric acid gas?
4. What would be the effect of boiling such a solution, and of continuing the process until the liquid had become reduced to a small bulk?
5. An ordinary wide-mouthed bottle is filled with hydrochloric acid gas and inverted over water; describe what you would expect to occur.
6. How is liquefied (anhydrous) hydrochloric acid obtained, and in what respects does it differ from gaseous hydrochloric acid?
7. Given caustic soda and hydrochloric acid, describe how you would prepare a sample of common salt.
8. What is the action of hydrochloric acid on (*a*) lime, (*b*) manganese dioxide, (*c*) zinc, (*d*) marble, (*e*) nitrate of lead? Give equations in each case representing the reactions.
9. Make a list of the properties or reactions of hydrochloric acid which you regard as *characteristic* of this body.
10. A solution of silver nitrate is added (*a*) to excess of dilute hydrochloric acid, (*b*) to a solution of common salt; in each case a white precipitate is formed; describe the nature of the precipitate and also of the substances to be found in the supernatant liquid.

CHAPTER VI.

PHYSICAL PROPERTIES OF GASES.

ALTHOUGH some of the earlier philosophers regarded air as a fluid, it was not till the seventeenth century that any definite proof of this was given. Nor was it till late in the eighteenth century that (with the exception of air, hydrogen and carbon dioxide) gases were distinguished from one another as different chemical substances. At the present day, and especially amongst the non-metals and their compounds, we are acquainted with a large number of bodies which exist under ordinary atmospheric conditions in the form of gas.

The examination of the properties of gases, and of the part which they play in chemical reaction, cannot be carried out without a knowledge of their physical properties.

We purpose then to show how the weight of a gas may be determined, having regard to the allowances to be made for temperature and pressure.

The General Property of Weight of Gases.

This may be shown in the following way—

Exp. 37.—Suspend two similar beakers of about 5 litres content, one of them in an inverted position, at the ends of the arms of a rough balance and counterpoise them. Now pass hydrogen into the inverted beaker by means of a tube held as far up the beaker as possible, but without coming into contact with it, and gradually lowering the tube towards the mouth of the beaker. The hydrogen will accumulate in the upper part of the beaker and gradually fill it to the mouth, pressing out the air before it.

The arm of the balance will at the same time be deflected, and the beaker in question will rise. Add small weights till the arm becomes horizontal again. If the beakers are of the size prescribed above, about 6 grammes will be necessary for this. If we continue to pass the gas after this, the equilibrium of the balance will not be disturbed, but on withdrawing the tube the arm bearing the inverted beaker will soon begin to fall again, showing that it is now gaining weight. This is due to the diffusion of the hydrogen out of the beaker and its replacement by air, and it will be seen how gradual such a process is.

We have seen then by this rough experiment that when 5 litres of air are replaced by 5 litres of hydrogen, a loss of weight occurs equal to about 6 grammes, which represents that a litre of hydrogen is approximately 1·2 grammes *lighter* than a litre of air.

Exp. 38.—When the whole of the hydrogen has been cleared out of the inverted beaker and replaced by air, pass carbon dioxide downwards into the other beaker, and note that it is depressed, showing that whilst hydrogen is much *lighter* than air, carbon dioxide is *heavier* than air. The weight required to restore equilibrium in this case will be found to be approximately 3 grammes.

To determine the weight of gases more accurately; suspend from the arms of a delicate chemical balance two globes fitted with stop-cocks, and having a content of about 500 c.c. In order to eliminate corrections for buoyancy of the air the two globes should be as nearly as possible similar.

Exhaust one of the globes carefully at the air-pump, and then close the stop-cock. Now attach it at one arm of the balance, and the other globe filled with dry air at the other arm, and note the weight to be added in order to bring it into equipoise. This will be the weight of 500 c.c. of air, say 0·618 gramme at the temperature and pressure prevailing at the time, say 9° C. and 750 m.m. pressure. Now attach the vacuous globe to a supply of dry hydrogen and again equipoise.

Instead of 0·618 gramme we find only 0·575, and we have the data necessary to determine—

(1) The relative density of hydrogen and air.

(2) The weight of a litre of hydrogen or air.

For the present we only know that one litre of air and of hydrogen at 9° C. and 750 m.m. pressure weigh respectively 1·236 grammes and 0·086 gramme.

We shall now consider the effect of temperature and of pressure on the volume and density of a gas.

Relation of Volume of Gases to Temperature.

Exp. 39.—Take one of the globes previously mentioned, and plunge it (with the stop-cock open) in a bath of water cooled down to 0° C. by the addition of fragments of ice. When it has remained some minutes, and the air in it has been reduced to zero, close the stop-cock and carefully dry the outside of the globe. The other globe is to be heated to 100° C. by steam or boiling water, the stop-cock is then closed, and the globe dried. Attach both to the balance, and the latter will be found to be considerably lighter than the other. The air in the globe owing to expansion has been partly expelled from the globe.

The expansion which a gas undergoes is a constant, and independent of the chemical composition of the gas. Dalton found *the expansion to be* $\frac{1}{273}$ *part of its volume at* 0° *for each increment of* 1° *C. in temperature.*

This is, however, more usually known as the Law of Charles. Stated in another form we have—

273 vols. of gas at 0° C. become 274 vols. at 1° C.
,, ,, ,, 275 ,, ,, 2° C.
,, ,, ,, 276 ,, ,, 3° C., and so on;
also ,, ,, ,, 272 ,, ,, −1° C.
,, ,, ,, 271 ,, ,, −2° C.
,, ,, ,, 270 ,, ,, −3° C.

Now the *absolute zero* of temperature is −273° C., and converting the temperatures stated above into degrees absolute by the addition of 273, we see that the volume of the gas will be—

At 270° absolute, 270 volumes
,, 271° ,, 271 ,,
,, 272° ,, 272 ,,
,, 273° ,, 273 ,, &c.,

that is, the volume of a gas is *directly proportional to its absolute temperature.*

Relation of volume of Gases to the pressure to which they are subjected.—An experimental investigation of this may be made by using the simple apparatus here described. A B C is a bent glass tube of even diameter, one limb of which is made at least 8 feet long, and the other, provided with a tap at the extremity, is 40 inches. A side tube is provided at B, for running off mercury from the longer limb. It is not necessary to graduate the tubes throughout, but the following points may be marked on the shorter limb—

(1) a point 4 inches from C.
(2) a point 6 inches from C.
(3) a point 12 inches from C.
(4) a point 24 inches from C.
(5) a point 39 inches from C.

And on the longer limb—

(6) a point 63 inches higher than the level of (5).
(7) a point 95 inches higher than the level of (5).

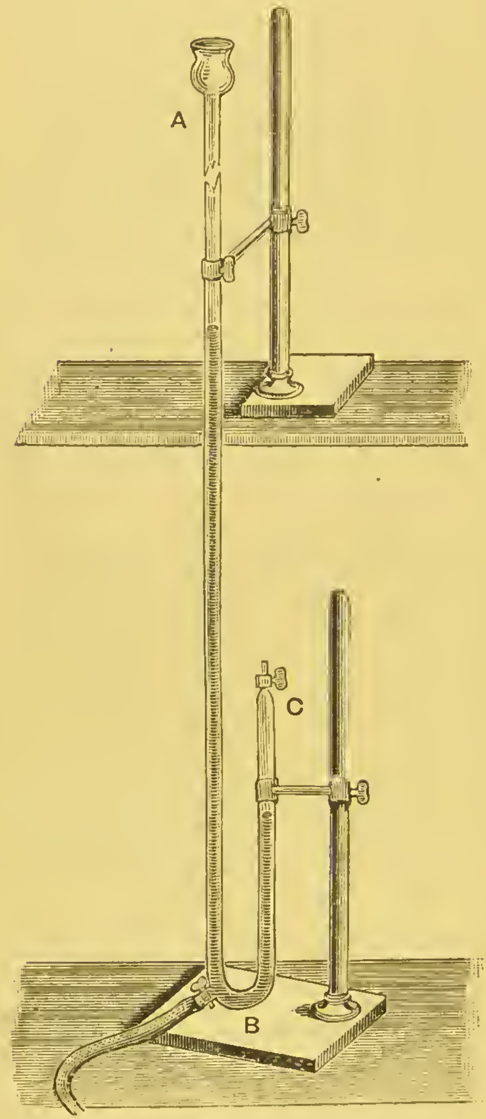

Fig. 9.

Open the tap and pour in mercury to the level (3), then close the tap, and allow mercury to run off till it falls to level of (4). The pressure to which the gas is subjected is now that of the atmosphere (say 30 inches of mercury, minus the column of mercury in the shorter limb that stands above the point (5), *i. e.* 15 inches of mercury). The length of the tube occupied by the gas is now 24 inches instead of 12 inches at the outset. The pressure on the gas originally to that exerted now is in the ratio 30 : 15, or 2 : 1, and the volume of the gas (the tube being of even diameter throughout) is in the ratio 12 : 24, or 1 : 2.

Now pour in mercury till it reaches the level of (6) in the longer limb, and we shall find that in the shorter limb it will then stand at level (2). The length of the tube occupied by the gas is now 6 inches, or the volume is in the ratio 1 : 2 of that which it originally occupied. The pressure is 60 : 30, or 2 : 1.

Finally pour in more mercury till the level (7) is reached in the longer limb, and we find that in the shorter limb it will stand at level (1). The length of the tube occupied by the gas is now 4 inches, or the volume is in the ratio 1 : 3 of that which it originally occupied. The pressure is 90 : 30, or 3 : 1.

That is, placing the respective ratios of pressures and volumes side by side we have—

Pressure increased, 1 : 2.	Volume decreases, 2 : 1
„ decreased, 2 : 1.	„ increases, 1 : 2
„ „ 3 : 1.	„ „ 1 : 3,

or *when the temperature remains constant the volume occupied by a gas is inversely as the pressure.* This is known as the law of Boyle from the fact that he first gave definite experimental proof of its truth in 1662. In France and Germany it is often called Mariotte's Law, Mariotte being credited with the independent discovery of the law fourteen years later than Boyle.

It may be expressed shortly by the formula—

$$P.\ V = \text{a constant.}$$

P being the pressure, and V the volume occupied by the gas under that pressure.

If the volume is taken as unity under a pressure of 1 atmosphere, the law may be stated thus—

$$P.\ V = 1.$$

The above description is only true for a perfect gas under moderate pressure and temperature. No perfect gas exists in reality: hydrogen, nitrogen, and a few other gases behave at ordinary temperatures and pressures nearly like a perfect gas, but at very low temperatures or high pressures even these no longer agree strictly with the laws as stated. It is found indeed that all gases when placed under certain extreme conditions of temperature and pressure, behave abnormally, and ultimately pass into the liquid state, and it is only when they are far removed from this liquid state (*i. e.* at temperatures and pressures such that they are far above the boiling-point of the liquid) that they obey Charles' and Boyle's laws.

Liquefaction of gases.—By a combination of high pressure and low temperature every gas can be liquefied.

The following table gives the temperatures and pressures at which some of the commoner gases become liquids—

Carbon dioxide at − 80° C. and 1 atmosphere pressure,
or at − 20° C. ,, 23 ,, ,,
or at + 20° C. ,, 58 ,, ,,
Sulphur dioxide at − 10° C. ,, 1 ,, ,,
or at + 10° C. ,, 2·3 ,, ,,
or at + 30° C. ,, 5·3 ,, ,,
Nitrogen at − 193° C. and 1 atmosphere pressure
or at − 160° C. ,, 14 ,, ,,
or at − 146° C. ,, 52 ,, ,,
Air at − 191° C. ,, 1 ,, ,,
or at − 140° C. ,, 39 ,, ,,
Ethylene at − 103° C. ,, 1 ,, ,,

A gas cannot always be liquefied by pressure alone. There is in fact a temperature peculiar to every gas *above* which the gas cannot be liquefied by any pressure whatever. Thus Andrews has shown that at temperatures above 31° C. it was impossible to liquefy carbon dioxide by pressure.

This temperature is called the *critical temperature* of the gas, so that the critical temperature of carbon dioxide is 31° C. The pressure which a gas exerts at its critical temperature is called the *critical pressure.* The following table gives these two constants for a number of gases—

	Critical temperature.	Critical pressure.
Nitrogen	− 146° C.	33 atmospheres.
Oxygen	− 119° C.	50 ,,
Nitric oxide	− 93° C.	71 ,,
Marsh gas	− 100° C.	50 ,,
Carbon monoxide	− 140° C.	39 ,,

It will be noticed that the five gases in the table have very low critical temperatures; these gases and hydrogen were until recently called *permanent* gases, because until 1879 all attempts to liquefy them had failed owing to the temperatures employed being above the critical point. Hydrogen has the lowest critical temperature of all gases,[1] and it has only recently been liquefied by Olszewski.

Various methods have been employed in liquefying gases. Faraday was able to liquefy a large number of gases by means of their own pressure in glass tubes. To liquefy chlorine in this way the yellow crystals of chlorine hydrate, $Cl_2\ 8\,H_2O$, are brought into a glass tube of about 1 c.m. in diameter, and closed at one end. The tube is then bent at right angles at about its middle point and sealed. If now the sealed end be placed in a freezing mixture, whilst the other end containing the hydrate be gently warmed, a comparatively large volume of chlorine is liberated, and the pressure of the accumulated gas together with the low temperature employed is sufficient to bring about its liquefaction.

If silver chloride be saturated with ammonia gas, it forms the compound $2\,AgCl.\ 3\ NH_3$, and this body treated in the same way evolves ammonia in such a quantity as to liquefy by its own pressure.

Diffusion of gases.—The particles of gases possess a much greater freedom of motion than do those of liquids or solids, for the excursions which they may make are confined in the case of the latter to the space occupied by the liquid or solid itself; in the case of gases, however, the extent of these excursions is only limited by the walls of the vessel in which they are contained. Furthermore, if the walls are loose and open in texture, that is, porous, then it is possible for the gaseous particles to traverse them.

If a quantity of ammonia be discharged at one end of a room, the odour of the gas will, after a short time, be perceptible at the other end, even though the temperature of the room is constant throughout and the air still and free from currents.

---

[1] The newly-discovered gas *helium* has resisted liquefaction even under conditions which were found sufficient to bring about the liquefaction of hydrogen.

That a very light gas should rise in a denser atmosphere and a heavy gas fall, is only what might be expected from the experience gained with solids or liquids. The following experiments will, however, serve to show that gases, however light they may be, will also gradually diffuse *downwards* through a denser atmosphere, and however heavy they may be, they will gradually diffuse *upwards* through a lighter atmosphere. The particles of a gas must therefore be subject to some other impetus than that accounted for by the ordinary laws of gravitation. The transfer of a mass of a gaseous body (hydrogen or coal gas in a balloon) takes place, it is true, in accordance with gravitation, but *diffusion* of the particles of gases cannot be so explained; it is the result of an active and incessant motion proper to the particles themselves.[1]

Exp. 40.—A stout glass collecting jar of about $\frac{1}{4}$ litre content is filled with hydrogen and held steadily, mouth downwards, for three or four minutes. A lighted taper is then brought into it, and it will be found that instead of burning quietly, as pure hydrogen does, there will be an explosion. This is evidence that during the period of exposure, the heavier air particles have diffused into the jar, the explosion being due to admixture of oxygen with the hydrogen.

Exp. 41.—Fill three similar bottles (wide-mouthed) with chlorine and close them with stoppers. Place them in beakers as shown and cover the mouth of the beaker with a glass plate; remove the stoppers from two of them and make the following observations.

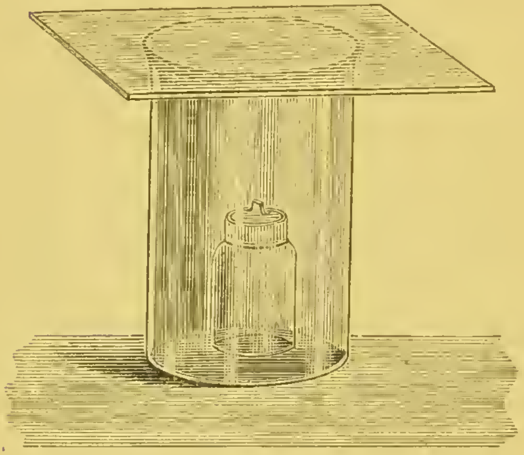

Fig. 10.

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[1] This statement must not, however, be taken to indicate that the constitution of gases differs essentially from that of liquids and solids. The *particles* of liquids and possibly solids also partake of progressive movements, but these are more limited in extent, being restricted to the mass of the liquid or solids; they also give evidence of being less rapid.

(1) In a few minutes aspirate some of the air from the beaker through a solution of potassium iodide; the solution will be coloured brown owing to the fact that chlorine liberates iodine from a solution of potassium iodide. Air will not do this, and evidence is thus presented that some of the chlorine, though more than twice as heavy as air, has passed from the bottle into the surrounding space.

(2) Compare the colour of the second unstoppered bottle from time to time with that of the one remaining stoppered, the green colour in the former will be seen to grow much more faint owing to the gradual diffusion of the chlorine from the bottle into the beaker.

Exp. 42.—A porous cell, such as is used in voltaic batteries, is fitted with an indiarubber stopper, and a glass tube about half a meter long, furnished with a bulb, is passed through the stopper; this is bent and drawn out into a jet as shown in the figure. Before inserting the cork fill the bulb and lower part of the tube with water. Now place a beaker filled with hydrogen over the porous cell, and the water will be immediately depressed and driven out of the jet in a fine stream. This is evidence that the light gas hydrogen passes through the walls into the porous cell quicker than the air is able to pass out of it. A greater volume of gas collects within the space of the cell and tube and forces the water out before it.

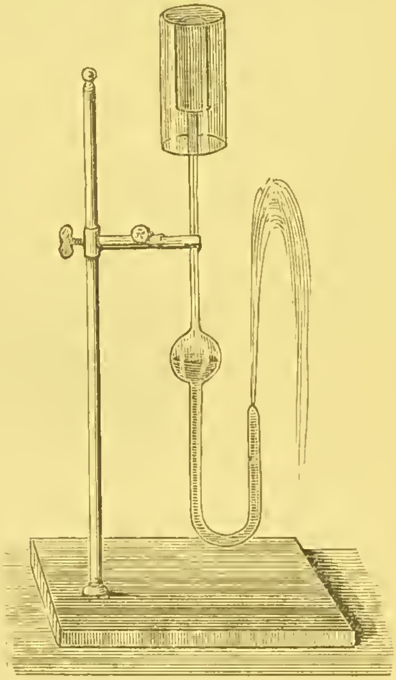


FIG. 11.

Exp. 43.—Do a similar experiment with the arrangement shown in the figure, in which it is possible to observe, by bubbles passing through the water in the bottle, that air is finding its way into the porous cell through the glass tube. In this case the cell containing air is surrounded with carbon dioxide in a beaker. Under such circumstances the air diffuses out of the cell quicker than the heavier gas, carbon dioxide, passes into it. This tends to produce a partial vacuum within the cell, and air enters in bubbles through the liquid in the bottle.

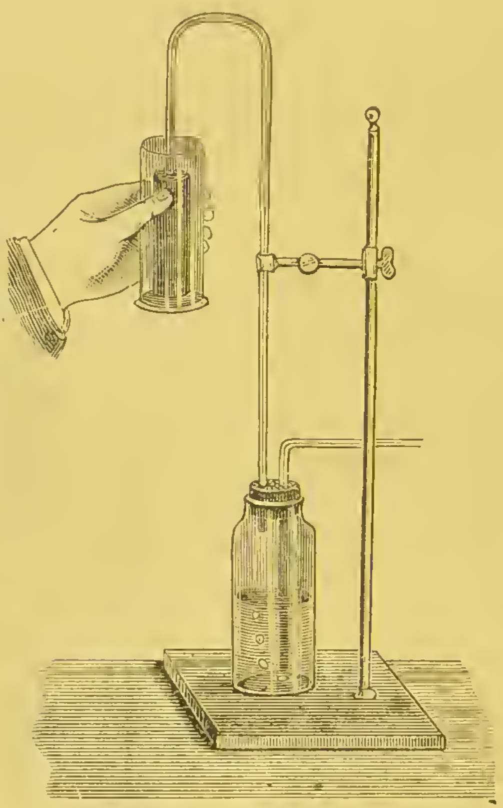


FIG. 12.

Exp. 44.—Repeat the last experiment, using oxygen instead of carbon dioxide, and note that in this case the bubbles pass in much more slowly, and altogether a much smaller volume of air is required to restore equilibrium in the cell.

The relative densities of the gases employed in the above experiments are—

Hydrogen, 1.	Air, 14·4.	Carbon dioxide, 22.
		Oxygen, 16.

The greater the difference in density, the more rapid is the diffusion. By measuring the amount of different gases which diffused through a porous plug in a given time, under like conditions, Graham found that *the relative rate of diffusion is inversely proportional to the square root of their densities.* Thus in relation to air—

		$\frac{1}{\sqrt{\text{density}}}$.	Velocity of diffusion observed.
Density of hydrogen	= 0·0695	= 3·792	3·830
„ oxygen	= 1·1043	= 0·951	0·949
„ carbon dioxide	= 1·5180	= 0.812	0·812

The Metric System of Weights and Measures.

Before entering into further detail in regard to the relative density of gases, it will be well to adopt certain units of mass and volume. The metric system has been found convenient for all operations in which weighing and measuring are concerned.

The *unit of length* in this system is the *metre*, which is equivalent to 39·37 inches.

The *unit of volume* is that of a cube whose side is $\frac{1}{100}$ of a metre, equivalent to very nearly one-sixteenth of a cubic inch, and the *unit of weight* is the weight of this volume of water, the temperature being that at which water has its maximum density, viz. 4° C. This weight is termed the *gramme*, and is equivalent to 15·432 grains.

The prefix *kilo* indicates the multiple 1000, thus—

1 kilogramme = 1000 grammes = 15432 grains = abt. 2·2 lbs.

The prefixes *deci*, *centi*, and *milli* respectively indicate the fractional parts $\frac{1}{10}$, $\frac{1}{100}$, and $\frac{1}{1000}$.

1 decimetre = $\frac{1}{10}$ metre = 3·937 inches.
1 centimetre = $\frac{1}{100}$ „ = 0·3937 „
1 millimetre = $\frac{1}{1000}$ „ = 0·03937 „

One inch is thus slightly more than 25 millimetres.

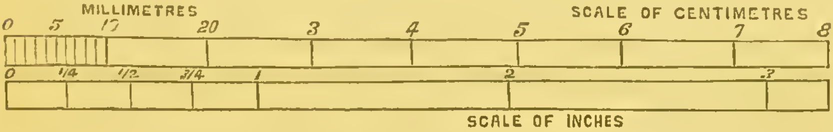


FIG. 13.

1 decigramme = $\frac{1}{10}$ gramme = 1·5432 grains.
1 centigramme = $\frac{1}{100}$,, = 0·15432 ,,
1 milligramme = $\frac{1}{1000}$,, = 0·015432 ,,

A measure of volume very frequently employed is the *litre*, which is the volume occupied by a kilogramme of water; it is therefore equivalent to a cubic decimetre, or, in English measure, 61·027 cubic inches.

Whenever the specific gravity of a liquid or solid is spoken of, water is used as the standard of comparison; thus, if we say that sulphuric acid has a specific gravity of 1·84, we imply that it is 1·84 times as heavy as water, and hence one cubic centimetre of such acid will weigh 1·84 grammes.

Hydrogen is in like manner employed as the standard by which to express the density (or better, specific gravity) of gases. One litre of hydrogen at standard temperature and pressure (*i. e.* 0° C. and 760 m.m. mercury) weighs 0·0899 gramme, and when we say that nitrogen has a density of 14, we mean that it is 14 times as heavy as hydrogen; one litre of it should therefore weigh (0·0899 × 14) grammes.

In calculations bearing upon the weight and volume of gases, it is convenient to bear in mind the volume occupied (at 0° C. and 760 m.m.) by a gramme of hydrogen; this is, of course, $\frac{1}{0{\cdot}0899}$ litres, or 11·12 litres.

The volume occupied by 1 gramme of nitrogen is $\frac{1}{0{\cdot}0899 \times 14}$ litres, and by 14 grammes of nitrogen $\frac{14}{0{\cdot}0899 \times 14}$ litres, that is again 11·12 litres.

And in general, the volume occupied by x grammes of an elementary gas, when x is the atomic weight of the element, is 11·12 litres. It must be added that sometimes *air* is taken as the standard of density; air is 14·383 times as heavy as hydrogen, and one litre of air at standard temperature and pressure weighs 1·293 grammes.

The constitution of gases.—Any views that may be held relating to the constitution of gases must be consistent with the following observations—

(1) No difference in physical character is found to exist between gases that are elements and those that are compounds. In either case they expand or contract, as the temperature and pressure vary, in accordance with the laws of Charles and Boyle. There is, indeed, every reason to believe that the constitution of simple and compound gases is similar.

(2) That the smallest portion of matter attainable by any process of subdivision or capable of taking part in a chemical change is not infinitely small (Dalton's atomic theory).

(3) Gay Lussac showed that when gases combine together they do so in volumes which bear a simple ratio to one another and to that of the product. The relative volumes which do so combine are also found to be represented by small whole numbers.

Thus actual experiment shows that—

2 vols. of hydrogen and 1 vol. of oxygen combine to form 2 vols. of water vapour.
1 vol. of hydrogen and 1 vol. of chlorine combine to form 2 vols. of hydrochloric acid gas.
2 vols. of carbon monoxide and 1 vol. of oxygen combine to form 2 vols. of carbon dioxide.
1 vol. of nitrogen and 3 vols. of hydrogen combine to form 2 vols. of ammonia.

that is

1 vol. of water vapour is formed from			1	vol.	of hydrogen and
			$\frac{1}{2}$	,,	,, oxygen.
1 ,,	hydrochloric acid	,, ,,	$\frac{1}{2}$	,,	,, hydrogen and
			$\frac{1}{2}$	,,	,, chlorine.
1 ,,	carbon dioxide	,, ,,	1	,,	,, carbon monoxide and
			$\frac{1}{2}$	,,	,, oxygen.
1 ,,	ammonia	,, ,,	$1\frac{1}{2}$	,,	,, hydrogen and
			$\frac{1}{2}$	,,	,, nitrogen.

Hence, for instance, whatever the smallest particle of hydrochloric acid may be, it contains both hydrogen and chlorine in equal volumes, and we shall have to assume the existence of still smaller particles of these elements.

Three striking and important features are thus evident—

(*a*) that the constitution of *all* gases is similar ;

(*b*) that the ultimate particles of matter have actual and definite dimensions ;

(*c*) that we must conceive of two kinds of particles.

Avogadro's hypothesis affords an explanation that is consistent with the behaviour of simple and compound gases, and at the same time in consonance with Dalton's theory of the indivisibility of the ultimate particle known as the atom.

Avogadro recognized two kinds of ultimate particles—

(*a*) the ultimate particle which can exist in the free state, as for instance the smallest particle of gaseous hydrochloric acid. This we term the *molecule.*

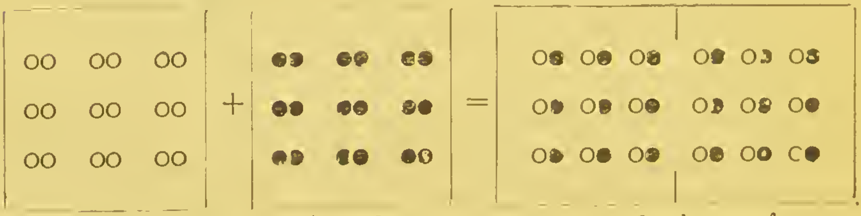
(*b*) the ultimate particle which is capable of taking part in a chemical change, or capable of being transferred from one chemical compound to another, as, for instance, the hydrogen or the chlorine contained in the molecule of hydrochloric acid. This we term the *atom.*

He also stated the hypothesis *that equal volumes of* all *gases at the same temperature and pressure contain the same number of molecules*, hereby affording a reasonable explanation of the similarity in physical characters exhibited by all gases whether they are simple (*i. e.* elements) or compound.

A diagrammatic method of representing the constitution of gases may serve to present these ideas in a clearer light.

The combination of hydrogen with chlorine may be represented aa shown below, where

oo represents a molecule of hydrogen.
o ,, an atom ,, ,,
●● ,, a molecule of chlorine.
● ,, an atom ,, ,,



1 volume of hydrogen } combines with { 1 volume of chlorine } forming { 2 volumes of hydrogen chloride

The volume represented is such as to be that occupied by nine molecules, but the explanation holds equally well whatever number of molecules might be taken.

Also representing the molecule of nitrogen by N_2
" " " hydrogen by H_2
" " " ammonia by NH_3
and taking for equal volumes the mean space occupied by 4 molecules

$$\left|\begin{array}{cc} N_2 & N_2 \\ N_2 & N_2 \end{array}\right| + \left|\begin{array}{cc|cc|cc} H_2 & H_2 & H_2 & H_2 & H_2 & H_2 \\ H_2 & H_2 & H_2 & H_2 & H_2 & H_2 \end{array}\right| = \left|\begin{array}{cc|cc} NH_3 & NH_3 & NH_3 & NH_3 \\ NH_3 & NH_3 & NH_3 & NH_3 \end{array}\right|$$

1 volume of nitrogen } combines with { 3 volumes of hydrogen } forming { 2 volumes of ammonia

Similarly

$$\left|\begin{array}{cc|cc} CO & CO & CO & CO \\ CO & CO & CO & CO \end{array}\right| + \left|\begin{array}{cc} O_2 & O_2 \\ O_2 & O_2 \end{array}\right| = \left|\begin{array}{cc|cc} CO_2 & CO_2 & CO_2 & CO_2 \\ CO_2 & CO_2 & CO_2 & CO_2 \end{array}\right|$$

2 volumes of carbon monoxide } combine with { 1 volume of oxygen } forming { 2 volumes of carbon dioxide

$$\left|\begin{array}{cc|cc} H_2 & H_2 & H_2 & H_2 \\ H_2 & H_2 & H_2 & H_2 \end{array}\right| + \left|\begin{array}{cc} O_2 & O_2 \\ O_2 & O_2 \end{array}\right| = \left|\begin{array}{cc|cc} H_2O & H_2O & H_2O & H_2O \\ H_2O & H_2O & H_2O & H_2O \end{array}\right|$$

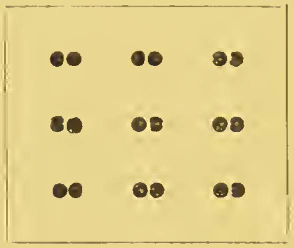
2 volumes of hydrogen } combine with { 1 volume of oxygen } forming { 2 volumes of water vapour

The conception of the constitution of simple and compound gases indicated in these diagrams will be found to accord with the observations of Gay Lussac, and the hypothesis of Dalton and Avogadro.

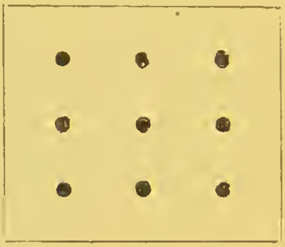
In the gases mentioned above it has been assumed that the molecule consists of two atoms, and though as a rule this assumption is borne out by the facts, there are certain exceptional cases in which it does not hold. Instances of this are afforded in the case of iodine vapour at very high temperatures, in which the molecule consists of *one atom ;* and sulphur vapour, just above the boiling point of sulphur (at 500° C.), in which the molecule consists of *six atoms.*

The representation of these cases may be made as follow—

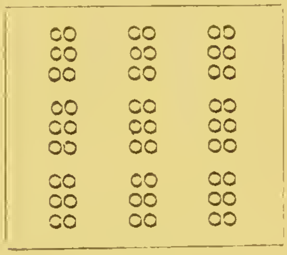
Iodine vapour at 450° C.



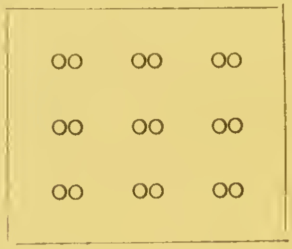
Iodine vapour at 1,500° C.



Sulphur vapour at 500° C.



Sulphur vapour at 1,000° C.



The vapours of Hg, Cd, P, and As are other examples of abnormal molecules, but the treatment of these is postponed to a later stage.

The molecular weight of gases.—In speaking of the density of gases, it is most usual to adopt that of hydrogen, the lightest of gases, as the standard of comparison, and to designate the density of hydrogen as unity. The density of gases can then be determined in the manner described at the beginning of this chapter. It will be found from actual experiment that

	Hydrogen being taken as		1·0
the density of	nitrogen	is	14·0
,, ,,	oxygen	,,	15·9
,, ,,	chlorine	,,	35·4
,, ,,	hydrogen chloride	,,	18·2
,, ,,	ammonia	,,	8·5
,, ,,	carbon dioxide	,,	22·0 and so on.

As equal volumes of the respective gases contain the same number of molecules, then the weight of the molecule must be *proportional* to that of the weight of equal volumes of the gases, *i. e.* proportional to the density.

The weight of the *atom* of hydrogen having been taken as 1, the *molecule* H_2 must be taken as 2. Hence the *molecular weight* of the other gases will likewise be doubled—

Molecular weight of	hydrogen	being taken as	2·0
,, ,,	nitrogen	will be	28·0
,, ,,	oxygen	,,	31·8
,, ,,	chlorine	,,	70·8
,, ,,	hydrogen chloride	,,	36·4
,, ,,	ammonia	,,	17·0
,, ,,	carbon dioxide	,,	44·0

and so on.

In writing equations to express chemical reactions regard must therefore be paid to the state in which the bodies concerned exist. If in the solid condition, the molecular structure is usually undefined, and a mere empirical statement of the quantity of the "reagent" employed must be made.

$$6\,S \qquad 3\,S_2 \quad \text{and} \quad S_6$$

all represent 192 parts by weight of sulphur. The first is the form used for expressing a certain weight of solid sulphur, the second expresses the same weight of sulphur in the form of vapour at 1000° C., and the third the sulphur in the form of vapour at 500° C.

So $H_2 + O = H_2O$

and $KClO_3 = KCl + O_3$

would be incorrect, since in the first equation free oxygen is employed, and we have learnt that in this state there are two atoms in the molecule, and in the second equation O_3 would indicate that ozone was the gas resulting from the decomposition of $KClO_3$: this is not the case. The correct forms of expression would be obtained by doubling the formulæ—

$$2\ H_2 + O_2 = 2\ H_2O$$

and

$$2\ KClO_3 = 2\ KCl + 3\ O.$$

SUMMARY.

1. *Relative weight* (or density) of gases ascertained by comparing the weight of the gas with that of an equal volume of hydrogen (or air) under the same conditions of temperature and pressure.
2. *Volume as influenced by variations of temperature and pressure.*

If t = temperature in degrees Centigrade

then $t + 273$ = " " absolute

$$V \text{ (volume at } 0° \text{ C.)} = v\,\frac{273}{273+t}$$

when v is volume observed at t° C.

If p = pressure in m.m. of mercury

then V (volume at 760 m.m. pressure) = $\frac{vp}{P}$ or $\frac{vp}{760}$

3. Gases may be liquefied by pressure, provided the temperature is sufficiently low, *i. e.* is lower than the "critical temperature."
4. Gases, whether elementary or compound, seem to be similarly constituted.

Gases combine together in volumes that bear a simple ratio (*e. g.* 1 : 1, 1 : 2, 2 : 3 and the like) to one another and to that of the product resulting from their combination.

Hence need for discriminating between *the atom* (the smallest particle of an element which can enter or be expelled from chemical combination), and *the molecule* (the smallest particle of an element or compound that can exist in the free state), and for the acceptance of Avogadro's hypothesis.

5. The molecule usually consists of 2 atoms, but iodine, sulphur, mercury, cadmium, phosphorus and arsenic, under certain conditions are exceptions to this rule.
6. For compounds in the gaseous condition the weights of the molecules are proportional to the densities of the gases, and indeed the molecular weight of hydrogen being expressed by 2 and its density (it being the unit of comparison) by 1, it follows that the molecular weight is double the density.
7. Formulæ and equations must be used with the understanding that they are a means of expressing, as far as possible, the condition of matter as well as its composition.

QUESTIONS.—CHAPTER VI.

1. What gases were known to the earlier chemists?
2. Describe an experiment showing that air has weight.
3. How would you determine the density of air as compared with hydrogen?
4. What would be the alteration in volume which a gas at normal pressure would undergo if submitted to a pressure of (*a*) 1140 m.m. (*b*) 190 m.m. of mercury?
5. The temperature of a gas at zero is raised to 91° C.; what change would there be in the volume of the gas?
6. What are the conditions necessary to bring about liquefaction of gases?
7. A beaker of carbon dioxide is left standing in air; what gases would you expect to find in the beaker after the lapse of a few minutes?
8. How do you explain the fact that a heavy gas will gradually pass *upwards* in an atmosphere consisting of a lighter gas, and *vice versâ?*
9. A porous cylinder (Exp. 42) is filled with hydrogen and exposed to an atmosphere of carbon dioxide; it is found that 20 c.c. of the hydrogen pass out of it in one minute. Using the same apparatus under similar conditions, but substituting oxygen for hydrogen, how much oxygen should pass out of the cylinder in the same period of time?
10. Given that a metre is 39·37 inches, calculate the number of cubic inches in a litre, and determine in the same measure the equivalent of 150 c.c.
11. A liquid has a specific gravity of 1·45, find the weight in grammes of 100 c.c. of it, and also the volume of it that will just weigh 100 grammes.
12. If a litre of hydrogen weighs 0·0899 grm., find the number of litres of it that will weigh 1 grm., and also the volume occupied by a gramme of oxygen.
13. Enunciate the hypothesis of Avogadro and state the evidence in favour of its acceptance.
14. Give instances of circumstances under which the vapour

density of iodine and sulphur are abnormal. How are these cases reconciled with Avogadro's hypothesis?

15. Taking the molecular weight of hydrogen as unit, write down the molecular weight of the following bodies in the gaseous condition:—nitrogen, chlorine, carbon dioxide, and hydrogen chloride.

16. Correct the equations—

$$
\begin{aligned}
&K_2 &&+ 2H_2O &&= 2KOH &&+ H,_2\\
2\,&SO_2 &&+ O_2 &&= 2SO_3, &&\\
&NaCl &&+ H_2SO_4 &&= Na_2SO_4 &&+ HCl,\\
&H_2O &&+ Cl_2 &&= 2\ HCl &&+ O.
\end{aligned}
$$

CHAPTER VII.

COMPOUNDS OF HYDROGEN WITH OXYGEN AND SULPHUR.

WATER.—When pure, water is a clear and tasteless liquid; under ordinary circumstances it may be regarded as colourless, but in reality it has a faintly bluish tinge, which is perceptible when white light is passed through a stratum of about 20 feet in thickness. It freezes at zero Centigrade, and boils under normal atmospheric pressure at 100° C., leaving no residue on evaporation. It is chiefly remarkable for its solvent properties, and there are few chemical substances which are not dissolved to some extent by water.

The chemical composition of water.

It is easily demonstrated (sce Exp. 45) that water is composed of hydrogen and oxygen, but this simple experiment gives us no information as to the proportions in which the hydrogen and oxygen combine; to ascertain these it will be necessary to carry out quantitative determinations, either by volume or by weight. If the determination by weight alone were made we could, knowing the relative density of hydrogen and oxygen, deduce the composition by volume, and *vice versâ*.

Exp. 45.—The fact that water is composed of hydrogen and oxygen may be shown by burning hydrogen in oxygen or air, and condensing the product of the combustion by holding a cool glass vessel over the flame. Moisture may be seen to form on the sides of the vessel, and in a little while this will run together into drops which will be found to show the properties of water. Not only hydrogen, but also bodies which contain hydrogen, such as coal gas and paraffin, when burnt give rise to the formation of water vapour, and hence the condensation of moisture often observed on the windows of a room.

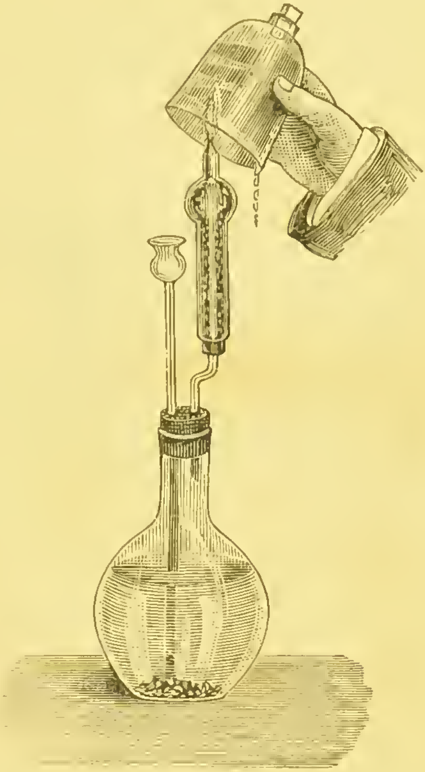


Fig. 14.

By such means it is established that water consists of hydrogen and oxygen. Further experiments are, however, necessary before we are able to say in what proportions the hydrogen and oxygen occur. In Chapter III. it has already been shown that water may be decomposed by heat, by the electric current, and by the action of certain elements. These processes are all based upon the *decomposition* of water, and they indicate that the hydrogen obtained from the decomposition of water is twice the volume of the oxygen contained in it. The volumetric composition of water may, however, be determined with much greater accuracy by a synthetical process.

Composition of water by volume.—The method employed at the present day, which we owe to Bunsen, is similar in principle to that employed by Cavendish in 1781, but capable of greater accuracy, and is moreover applicable to gases in general.

A tube of even bore, about 700 millimetres in length, is used.

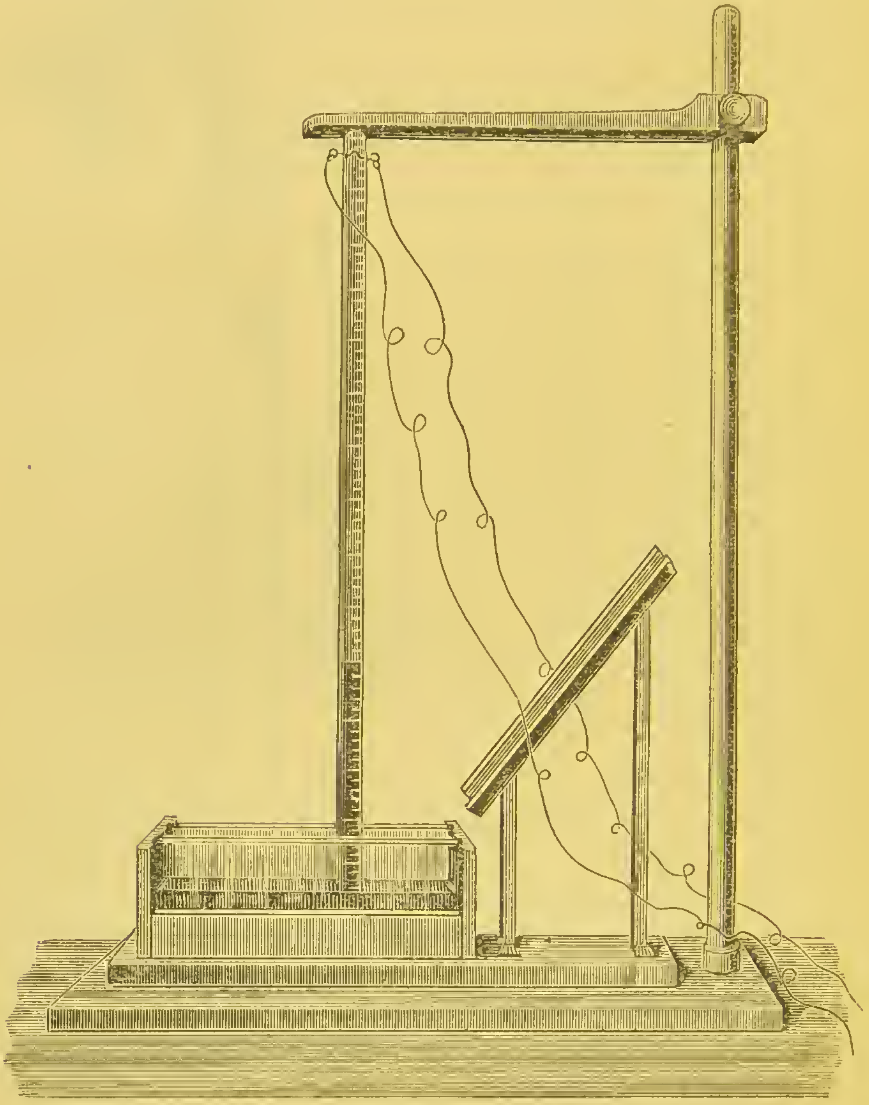


Fig. 15.

This is furnished with platinum wires to enable the gases to be "sparked," and millimetre divisions are etched on the tube. The "endiometer," as such a tube is called, is first calibrated so that its relative volume down to any given graduation is known. It is then moistened on the inside with a few drops of water, filled with mercury and inverted in a trough containing mercury. Pure oxygen about one-tenth of its volume is now passed in, and the exact level of the mercury in the eudiometer and in the trough is read. Hydrogen is then added equal to about six or seven times the volume of the oxygen. The eudiometer is now closed by pressing it down firmly on an india-rubber cushion at the bottom of the trough, and the spark is passed.

Under these circumstances the whole of the oxygen enters into combination with hydrogen, and as the water which forms condenses, a partial vacuum is formed inside the tube, and on gently raising it from the cushion the mercury is seen to rise.

From the observations taken we know

(*a*) the amount of oxygen ;
(*b*) ,, ,, hydrogen originally taken and that remaining over, the difference between these representing that which has combined with the oxygen.

An examination of these numbers will show that the volume of the hydrogen is double that of the oxygen with which it has combined.

If we surround the eudiometer with a steam-jacket[1], so as to prevent the condensation of the water, we shall be able to ascertain that the volume of the water vapour produced is exactly that of the hydrogen it contains. We may summarize these facts in the statement—*Two volumes of hydrogen combine with one volume of oxygen to form two volumes of water vapour or steam.*

Cavendish in 1781 was the first to ascertain the composition of water. He introduced a mixture of two volumes of hydrogen and one of oxygen into a strong glass vessel fitted with two wires, which passed into the inside of the vessel so as nearly to touch one another. The electric spark was passed by means of the wires, and the gases exploded. By repeating the experiment many times, he was able to show that oxygen combines with twice its volume of hydrogen, and that the liquid resulting from the combination was water.

---

[1] In this case omit the previous moistening of the eudiometer.

Composition of water by weight.—Many oxides, such as those of lead, copper, iron, etc., when heated in a current of hydrogen give up their oxygen, and are "reduced," as it is termed, to the metallic condition. In this reduction the oxygen combines with hydrogen with the production of water. If, then, we can ascertain (1) the weight of the water formed, and (2) the weight of the oxygen which has gone to form it, we shall have by difference the weight of the hydrogen contained in the water, and thus a full synthesis of water by weight. (See Exp. 61.) Very careful experiments have been performed in this way, using oxide of copper (CuO) as the medium for the supply of the oxygen. The equation expressing the reaction is—

$$CuO + H_2 = Cu + H_2O.$$

Experiments carried out in this way with extreme care indicated that one part by weight of hydrogen combines with 7·98 parts by weight of oxygen to form water.

Water of crystallization.—Many salts, when they are allowed to crystallize from solution, contain water, which is associated with them in definite proportions, and it cannot be regarded otherwise than as water *in combination* with the salt.

There is, however, very little stability in the combination; for instance, copper sulphate crystallizes with the composition $CuSO_4 . 5\,H_2O$. At 100° C. 4 H_2O are set free, and the remaining molecule of water requires a temperature of 240° C. to liberate it.

Alum crystallizes with 24 H_2O, 10 H_2O separate at 100° C., a further 9 H_2O at 120° C., and nearly the whole of the remainder at 280° C. In some cases, indeed, such as crystallized sodium carbonate or washing soda, $Na_2CO_3 . 10\,H_2O$, the salt loses water or *effloresces* at ordinary temperatures in a dry atmosphere.

The amount of water of crystallization which attaches itself to a salt varies according to the temperature at which the crystals form. Thus, from a solution of sodium sulphate, crystals of $Na_2SO_4 . 7\,H_2O$ can be obtained at temperatures below 26°, or crystals of $Na_2SO_4 . 10\,H_2O$ (Glauber's salt) at temperatures below 34°: while above 34° crystals of Na_2SO_4 are obtained. Epsom salt $MgSO_4 . 7\,H_2O$ furnishes another example giving $MgSO_4 . 6\,H_2O$.

Frequently, salts which at ordinary temperatures separate from solution in the anhydrous condition, possess water of crystallization when crystallized at low temperatures. Thus if a concentrated solution of common salt be allowed to stand at ordinary temperatures crystals of NaCl are obtained, but at – 10° C. crystals of $NaCl. 2 H_2O$, and at – 23° C. crystals of $NaCl. 10 H_2O$ separate: compounds like the two last are called *cryohydrates.*

Hydrates or hydroxides.—These possess a higher degree of stability, and in some cases are not decomposed even at very high temperatures. Thus, from caustic soda, which we may regard as $Na_2O. H_2O$, we cannot separate the water at all by heat, nor is it possible to do so in the case of caustic potash. Lime (CaO), when moistened with water, forms $CaO. H_2O$ or $Ca(OH)_2$, with the evolution of much heat, and the water is only separated again at a dull red heat.

Similarly, $SO_3 + H_2O$ form the very stable body sulphuric acid, H_2SO_4, which may be regarded as the hydrate of sulphur trioxide, and $P_2O_5 + 3 H_2O$ forms $2 H_3PO_4$, phosphoric acid.

SULPHURETTED HYDROGEN.—This is a gaseous body occurring in solution in certain mineral waters, and formed during the putrefaction of animal and vegetable matters which contain sulphur. It is a colourless gas with a disagreeable odour, and is poisonous if inhaled in quantity. It burns in a free supply of oxygen or air, forming water vapour and sulphur dioxide, whilst in a limited supply of air free sulphur is formed.

Water at 0° C. and 760 m.m. pressure dissolves 4·37 times its volume of the gas, and at 20°, 2·9 times its volume, the solution possessing the characteristic smell of the gas, and having a faintly acid reaction. The gas is decomposed by heat, the hydrogen it contains being set free, whilst in presence of many metals the sulphur combines with the metal.

Preparation of the gas.—Place in a small flask ferrous sulphide, fit the flask with a two-holed cork through which pass a thistle funnel and delivery-tube, and connect with a flask containing a little water to retain impurities carried over. The whole arrangement is shown in the figure. When the gas is required, pour about 50 c.c. of dilute sulphuric acid down the thistle funnel. The reaction is—

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Ferrous sulphide usually contains free iron, and the sulphuretted hydrogen prepared from it is thus contaminated with hydrogen—

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

The gas may be obtained in a purer condition by the action, aided by heat, of *concentrated* hydrochloric acid on sulphide of antimony according to the equation—

$$Sb_2S_3 + 6\,HCl = \underset{\text{Antimony trichloride.}}{2\,SbCl_3} + 3\,H_2S.$$

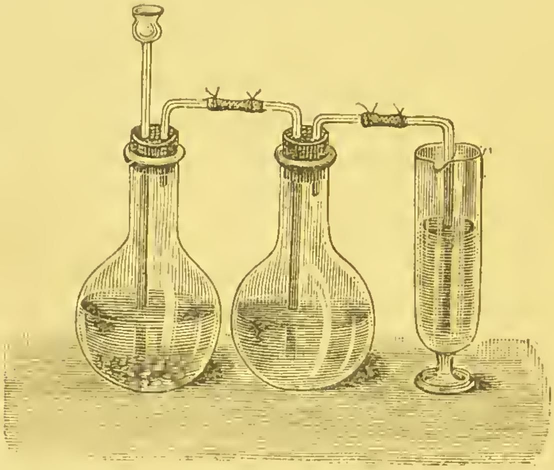


Fig. 16.

Exp. 46.—Make a solution of the gas in water, and dip in it a blue litmus paper, it will be slightly reddened. Note the odour of the solution.

Pour a few c.c. of it into neutral solutions of copper sulphate, lead nitrate, nickel sulphate, zinc sulphate, calcium chloride, sodium chloride. The following results will be noticed—

With copper sulphate, a dark brown precipitate of cupric sulphide:

$$CuSO_4 + H_2S = \underset{\text{Cupric sulphide.}}{CuS} + H_2SO_4.$$

With lead nitrate, a dark brown precipitate of lead sulphide:

$$Pb(NO_3)_2 + H_2S = \underset{\text{Lead sulphide.}}{PbS} + 2\,HNO_3.$$

With nickel sulphate, a dark brown precipitate of nickel sulphide:

$$NiSO_4 + H_2S = \underset{\text{Nickel sulphide.}}{NiS} + H_2SO_4.$$

With zinc sulphate, a white precipitate of zinc sulphide:

$$\underset{}{ZnSO_4} + H_2S = \underset{\text{Zinc sulphide.}}{ZnS} + H_2SO_4.$$

In the case of calcium chloride and sodium chloride there will be no precipitate, owing to the fact that the sulphides of calcium and sodium are readily soluble in water.

Now add some hydrochloric acid to the tubes containing the precipitates, and the sulphides of nickel and zinc will be found to dissolve, whilst those of copper and lead will remain.

By such a method we may prepare many of the sulphides of the metals, and we shall find them divisible into the following classes—

(1) Sulphides insoluble in water and dilute mineral acids.
(2) Sulphides which are insoluble in water, but soluble in dilute mineral acids.
(3) Sulphides which are soluble even in water.

The precipitate may be separated by filtration from the solution which remains, and it is possible in this way to separate any member or members of one of these classes from those of another class.

Many of the sulphides may also be prepared by mixing the metal (preferably in a finely divided condition or in filings) intimately with excess of powdered sulphur and heating in a porcelain crucible until the portion of sulphur over and above that which will enter into combination with the metal is volatilized. Access of air or of gases which may act upon the sulphide is to be avoided.

Exp. 47.—Sulphuretted hydrogen is, as we have seen, very soluble in water, and it attacks mercury; also, owing to its offensive nature, and to the fact that it is only slightly heavier than air, it should not be collected by displacement of air. We may, however, collect it over hot water, the solubility of gases being in general smaller the higher the temperature of the solvent. Having obtained a cylinder of the gas by collecting in this way, apply a lighted taper to the mouth, and note that the gas burns with a pale blue flame, and that a gas (SO_2) is formed which has the suffocating odour of burning sulphur—

$$2\ H_2S + 3\ O_2 = 2\ SO_2 + 2\ H_2O.$$

There is usually a slight deposit of sulphur on the sides of the vessel due to the cooling of the gas, and the difficulty of access of air in sufficient quantity to ensure complete combustion. If the taper be passed within the cylinder in which the gas is burning, it will be extinguished, showing that sulphuretted hydrogen, like hydrogen, burns in air (or oxygen), but does not support the combustion of a taper.

Exp. 48.—Detach the preparation flask, and fit it with a tube about 20 centimetres long, and drawn out to a fine jet. The gas may be lighted at the jet when all the air is expelled, and the presence of water in the products of combustion may be shown by holding a cool glass vessel over the flame. Also, by depressing the lid of a porcelain crucible into the flame, a deposit of sulphur may be obtained. Now heat the tube some distance away from the orifice with a Bunsen burner or spirit-lamp, and the gas will be decomposed by the heat, and a deposit of sulphur will form a little beyond the point where the heat is applied. Finally, extinguish the flame, and allow the gas to impinge on a piece of filter-paper moistened with nitrate (or acetate) of lead, a dark stain will be produced owing to the formation of sulphide of lead; by this test the presence of sulphuretted hydrogen may be detected even when present in very small quantities.

Tests for Sulphides.—(1) Warm the substance with dilute sulphuric acid; *most* sulphides are decomposed with the evolution of sulphuretted hydrogen, *e. g.*—

$$\underset{\text{Zinc sulphide.}}{ZnS} + H_2SO_4 = \underset{\text{Zinc sulphate.}}{ZnSO_4} + H_2S.$$

The sulphuretted hydrogen may be detected by its odour or by its action on paper moistened with a solution of acetate of lead, $Pb\ (C_2H_3O_2)_2$.

(2) Mix a little of a dry sulphide with sodium carbonate and heat strongly on charcoal with the blowpipe flame. Sulphide of sodium is formed, and may be recognized by the fact that when a little of the product is placed on a silver coin and moistened, a brown stain is produced. All sulphides react in this way.

SUMMARY.

1. That water is composed of hydrogen and oxygen is shown—
   (*a*) by burning or exploding hydrogen with oxygen or air;
   (*b*) by methods of decomposition of water (see Chap. III.).
2. That the hydrogen and oxygen combine to form water in the proportions 2 : 1 by volume and 1 : 8 (approx.) by weight is established—
   (*a*) by exploding hydrogen with excess of oxygen in a eudiometer;
   (*b*) by heating certain oxides in a current of hydrogen.
3. Water + certain basic oxides = hydroxides.
   „ + „ acidic „ = hydrogen salts or acids.
   Water of crystallisation attached to salts.
4. *Sulphuretted hydrogen*—
   Preparation.—By acting on sulphide of iron (or other sulphides) with mineral acids.
   Properties.—
   (*a*) Odour and solubility in water.
   (*b*) Decomposition by heat.
   (*c*) Burns in air forming H_2O and S or H_2O and SO_2.
   (*d*) Action on solutions of salts.
   (*e*) Nature of sulphides.

QUESTIONS.—CHAPTER VII.

1. Write down in separate paragraphs (*a*) the physical, (*b*) the chemical properties of water.
2. Under what circumstances does hydrogen combine with oxygen to form water?
3. Make a list of those properties of water which you regard as being absolutely characteristic of that body.
4. Give briefly two methods by which it may be shown that water is composed of hydrogen and oxygen in the proportions of two volumes of the former to one of the latter.
5. Pure hydrogen is passed over heated oxide of copper, and the water which forms is collected; if the loss in weight of the oxide of copper be 4·20 grammes, and the weight of the water obtained 4·73 grammes, determine the amount of hydrogen and oxygen in 100 grammes of water.
6. Define, with examples, what is meant by water of crystallisation. What is the nature of the compounds known as *hydroxides?*
7. How is sulphuretted hydrogen prepared? Write down the equation to show the action of hydrochloric acid on ferrous sulphide.
8. What products are obtained by burning sulphuretted hydrogen (*a*) in a limited supply of air, (*b*) in excess of air?
9. How would you show that sulphuretted hydrogen contains hydrogen and sulphur?
10. What is the action of sulphuretted hydrogen on acid solutions of (*a*) silver nitrate, (*b*) copper sulphate, (*c*) lead nitrate? Give equations showing the changes which take place.
11. How is sulphuretted hydrogen collected?
12. What is a sulphide? State the different processes by which sulphides may be prepared.
13. How would you detect the presence of a sulphide? Why is a paper moistened with acetate or nitrate of lead blackened in presence of sulphuretted hydrogen?

CHAPTER VIII.

PROPERTIES OF WATER—NATURAL WATERS.

Physical properties of water.—Water occurs not only in the liquid form, but also in the solid form, as ice or snow, and in the gaseous form, as water vapour or steam. Below 0° C. it takes the solid form, and above 100° C., at standard pressure,[1] it passes into steam; but at lower temperatures, however, water evaporates slowly into the air, and even in the solid condition, as snow and ice, evaporation goes on, though still more slowly. Water possesses a high specific heat, and is adopted as the unit with which other bodies are compared; ice has the specific heat 0·5, and steam 0·48.

Changes of volume of water at different temperatures.—When ice melts, the water which it forms is smaller in volume by nearly 10 per cent. than the ice from which it is formed. Also, as the temperature rises from 0 to 4° C. a further contraction, amounting however only to about $\frac{1}{100}$ per cent., occurs. At 4° C. water has its maximum density (and hence smallest volume), and above this it expands again as the temperature rises, until at 100° C. it occupies a volume rather over 4 per cent. greater than that at its maximum density. Water vapour has $\frac{1}{1240}$ the density of liquid water, and the volume of steam at 100° is nearly 1,700 times that of the water from which it is formed.

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[1] For further information concerning the tension of water-vapour and the boiling-point of water consult text-books on physics.

Latent heat of water and of steam.—When heat is imparted to ice it melts, but the thermometer continues to record 0° C. until the whole of the ice is melted, and when water is boiled the temperature of the water remains at 100° C., until it is wholly transformed into steam; moreover, the steam resulting also shows the temperature of 100° C. Although heat is being continually imparted to the ice or water, as the case may be, the thermometer records no increment of temperature. This heat is termed *latent*, for although it is undoubtedly communicated to the ice or water, it is unrecognized by the thermometer. The following experiments will afford convincing evidence on this point.

Exp. 49.[1]—Mix 100 c.c. of water at 0° C. with 100 c.c. of water at 80° C., stir quickly together, and the temperature of the resulting 200 c.c. of water will be found to be 40° C. (or rather less, in point of fact, owing to radiation of heat during the experiment).

Now mix 100 grammes of snow or powdered ice with 100 c.c. of water at 80° C.; the snow will just all melt, and the result will be 200 c.c. of water at 0° C.

In order to compare the results of these two experiments, we must adopt a unit of heat; this is defined as that amount of heat which will raise one gramme of water 1° C. in temperature, and it is termed a *calorie*. Since in the former experiment we have as an end result 200 grammes of water at 40° C., and in the latter 200 grammes at 0° C., there is a difference of 8,000 calories in the results as recorded by the thermometer. This amount represents the *latent heat* of fusion of 100 grammes of water in the solid state (snow), and for one gramme the value would be 80. That is to say, that as much heat is needed to melt one gramme of ice or snow as would raise one gramme of water from 0° C. to 80° C. (See also Exps. 15 and 16, Chap. II.)

This property is not peculiar to water, for, as a rule, when a change of physical condition occurs in any substance by the passage from the solid to the liquid state, similar phenomena can be observed. Frequent instances of it occur when salts, such as ammonium nitrate, calcium chloride, etc., are dissolved in water.

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[1] A simple form of calorimeter for this and similar experiments may be made of thin brass or copper standing on cork supports.

When the change takes place in the inverse manner, *i. e.* the passage from liquid to solid state, *heat is given out* equal in amount to that which, in the former case, had been rendered latent, and indeed the latent heat of steam is most readily ascertained by determining in this way the heat given out on the condensation of steam.

Similarly, the conversion of other liquids into vapour is accompanied by a large absorption of heat; a few drops of ether placed on the hand quickly evaporate and give rise to a sensation of great cold, the heat requisite for the transformation into vapour being abstracted from the hand.

And in general, whenever a change occurs in which the particles partake of a freer motion, heat really does disappear *as heat*, it being converted into energy of motion which is communicated to the particles.

So when the reverse change occurs, the energy of motion is converted back again into heat and reappears as such.

Freezing mixtures.—By dissolving a quantity of many salts such as ammonium nitrate or potassium iodide in water, a considerable depression of temperature may be obtained, but the freezing mixture most commonly employed is a mixture of common salt and snow or powdered ice, by which a temperature as low as − 23° C. may be reached.

The cooling is due to the fact that snow and salt when mixed, rapidly pass into the liquid condition, a change which we have seen is accompanied by an absorption of heat. The heat so absorbed in the passage from the solid to the liquid state is abstracted from the mixture, and hence the depression of temperature.

Any depression below − 23° C. would result in the separation of the solid cryohydrate $NaCl. 10\ H_2O$ (see page 57) with an *evolution* of heat which would counteract the cooling. The limit of temperature that can be attained by the use of salt and snow is therefore − 23° C.

Water as a solvent.—Most of the solid substances and gases which we meet with in chemical operations dissolve to an appreciable extent in water; some liquids, such as alcohol and sulphuric acid, associate themselves with water in all proportions; whilst others, such as oils, if shaken up with water separate again, being taken up by the water either only to a slight extent or not at all.

Solubility of solids.—The extent to which solid substances are soluble in water under similar circumstances varies according to the nature of the substance.

Minerals, such as coal, limestone, quartz, and many chemical compounds, such as sulphate of lime, oxide of lead, sulphide of iron, are only very slightly soluble, whilst others, *e. g.* nearly all chlorides and nitrates, are freely soluble. In any case, however, there is a limit to the amount of solid matter which can be dissolved, and when water has taken up as much as it will, we have what is known as a *saturated* solution.

The quantity of a substance required to form a saturated solution is usually greater the higher the temperature, though there is no simple general relation between the temperature and the amount dissolved.

The solubility in parts per 100 by weight of water is given for a few substances in the following table—

	0° C.	20° C.	50° C.	100° C.
Potassium nitrate ...	13·3	31·2	85·0	246·0
Sodium chloride ...	35·5	36·0	37·0	39·6
Potassium chlorate ...	3·3	8·0	19·0	58·0
Sodium chlorate ...	81·9	99·0	136·0	232·6
Mercuric chloride ...	5·7	7·4	11·3	54·0
Potassium sulphate ...	8·3	12·5	17·0	26·0

Solubility of gases.—There is no general connection between the solubility of gases and their chemical composition. Some gases, such as nitrogen, hydrogen, and carbon monoxide, are very slightly soluble, whilst others, such as ammonia, sulphur dioxide, and hydrochloric acid, are very freely soluble in water. The solubility, instead of increasing with the temperature, *decreases*, though in no simple relation. One volume of water at the temperatures stated, and under 760 m.m. pressure, dissolves the volumes of the respective gases given in the following table—

	0° C.	10° C.	20° C.
Nitrogen	0·020	0·016	0·014
Oxygen	0·041	0·033	0·028
Hydrogen	0·019	0·019	0·019
Carbon dioxide	1·799	1·185	0·901
Sulphuretted hydrogen ...	4·371	3·586	2·905

As instances of much more soluble gases we may take—

Sulphur dioxide	79·8	56·6	39·4
Hydrochloric acid ...	503·0	475·0	444·0
Ammonia	1049·6	812·8	654·0

The influence of pressure on the solubility of gases.—The volume of a gas which dissolves in water is directly proportional to the pressure (Henry's Law). Thus water at 0° C. dissolves of carbon dioxide—

At 1 atmosphere pressure 1·8 times its volume.
„ 2 atmospheres „ 3·6 „ „ „
„ 4 „ „ 7·2 „ „ „
„ $\frac{1}{2}$ atmosphere „ 0·9 „ „ „
„ $\frac{1}{3}$ „ „ 0·6 „ „ „

Soda-water is water charged with carbon dioxide under a pressure of about 4 atmospheres, and so long as this pressure on the surface of the water is maintained this volume of gas will be retained, but directly the pressure is released an effervescence is observed, and gas escapes from the liquid in proportion to the diminution of pressure.

Natural waters.—The water which evaporates from the surface of sea and land, and passes as water vapour into the air, is the purest form of natural water, and it retains its purity until it begins to fall as drops from the rain cloud.

Rain water.—When this is collected at the surface of the earth it has passed through a considerable stratum of air, and dissolved in its passage not only gases normally occurring in the atmosphere, but also such impurities as are found there. Even then the solid matter contained in it does not amount normally to more than 3 or 4 parts per 100,000. In the neighbourhood of towns the impurities taken up are more numerous and in larger quantity; also near the sea, and especially during high winds, much sodium chloride is found in rain water.

River water.—The composition of this water will of course depend on the nature of the surface and of the strata over which the water passes. For instance, a considerable part of the drainage area of the Thames consists of chalk, and its water contains about 30 parts of dissolved matter in 100,000, two-thirds of this consisting of calcium carbonate and sulphate, whilst the Dee in Scotland, passing over the older strata (principally slate and sandstone), contains only 5·6 parts of dissolved matter per 100,000, one-fourth of this being calcium salts. Since the water which passes into rivers collects from the surface of the soil, it contains also much more organic matter and carbon dioxide than rain water, arising from contact with plants and decaying vegetable matter.

Spring water.—The water of springs is rain water which has percolated through soil and rocks. The composition of spring waters varies very considerably, according to the depth from which the water rises, and the nature of the strata which it has traversed. In some cases the amount of dissolved matter is very large, and such springs, especially when they have a saline taste or medicinal properties, are known as *mineral* springs.

The springs of Bath and Harrogate contain magnesia and sulphuretted hydrogen, and are known as magnesia and sulphur waters; a spring near Woodhall Spa contains free iodine; many springs contain iron, and are known as *chalybeate* waters.

Mineral springs which rise from great depths are frequently hot, some having a temperature of nearly 100° C.; this is especially the case in volcanic regions, where the earth's temperature rises more rapidly with increase in depth below the surface.

Spring water is bright and sparkling, since it is more fully charged with gases than either rain or river water, and contains less organic matter this being removed in its passage through beds of soil or gravel. The composition of some typical waters is given in the table further down.

Sea water.—The matters dissolved or suspended in river or spring water are carried to the sea and remain there, since the water vapour rising from the sea consists of practically pure water. So that notwithstanding the removal of large quantities of these impurities by settling out or by the action of organisms, sea water is still the most impure form of natural water, and owing to the large amount of matter in solution its specific gravity is on the average 1·03. In those land-locked seas which receive much river water the impurities are of course in smaller quantity, but in the open ocean the residue obtained on evaporating 100,000 parts of sea water amounts to about 3,600 parts, of which nearly four-fifths is sodium chloride, the rest being chiefly calcium and magnesium sulphate and magnesium chloride. The peculiar taste of sea water is due to the presence of these salts.

In the following table details are given of the composition of some typical natural waters, the solids in parts per 100,000, the gases in cubic centimetres per litre—

COMPOSITION OF SOME NATURAL WATERS.

	SOLIDS.					GASES.		
	Total Residue.	Calcium Salts.	Magnesium Salts.	Sodium Chloride.	Organic Matter.	N.	O.	CO_2
Rain Water	3·4	*nil.*	*nil.*	0·5	1·0	13·1	6·4	1·3
River Water (Thames)	29	20	1·8	2·6	3·4	15·0	7·4	30·3
River Water (Dee)	5·6	1·4	0·5	1·0	2·2			
Spring Water	20			2·0	Traces	15·8		1·0
Mineral Water (Bath)	236	137	28	34	Traces	4·0	8·0	29·0
Sea Water	3,500	140	530	2.650	Traces	2·1	6·0	17·0

Chemically pure water may be obtained by distillation, the water being boiled and the steam which is given off condensed. On a small scale the apparatus shown (Fig. 13) may be used. The water is boiled in a flask connected with a condenser, through which a continual stream of cold water passes for the purpose of condensing the steam.

A small quantity of volatile organic matter may be carried over during a first distillation, and soluble matter from the glass condenser and receiver may be present: but on adding a few drops of potassium permanganate solution, and distilling again in platinum apparatus, very pure water is obtained.

Drinking water.—When water is to be used for drinking purposes, it is of the highest importance that it should be clear and colourless, and as free as possible from organic impurity arising from sewage contamination, or contact with decaying animal or vegetable matter. Dissolved salts, such as ordinarily occur in natural waters, are of less moment than organic impurity, and even such minute quantities as 0·3 or 0·4 per 100,000 may be injurious. The taste of drinking water is also an important factor, and whilst distilled water and rain water are flat and insipid, owing to the smaller quantity of dissolved gases which they contain, spring water has a characteristic freshness which renders it most palatable.

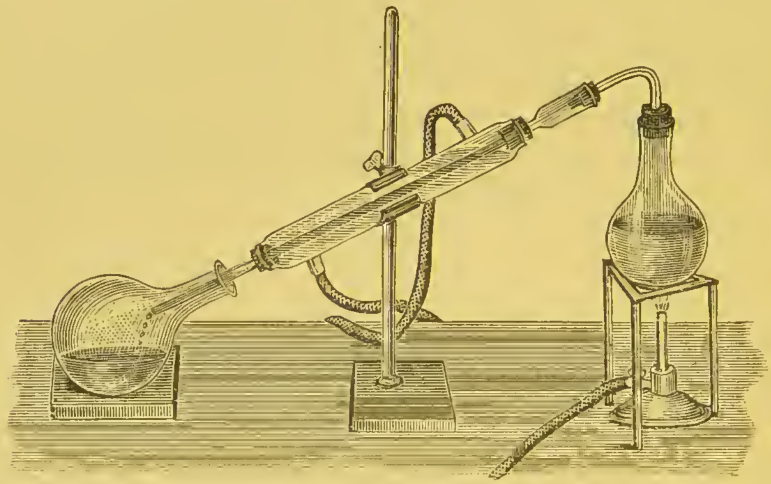

FIG. 17.

Hardness of water.—It is a matter of common experience that the sensation felt when washing the hands differs with waters from different sources. With rain water or the waters derived from sandstone areas a lather quickly forms, whilst with calcareous waters there is a sense of harshness, and a good deal of soap is required to produce a lather; we notice further that in the latter case a scum is formed which floats on the surface of the water. Waters that readily form a lather are known as *soft* waters, whilst those which do not are called *hard* waters. Hard waters contain much dissolved matter, and especially salts of lime or magnesia, which are the chief cause of the hardness.

The cleansing action of soap is due to the alkali and fatty acids which it contains, and no lather begins to be produced—or in other words no soap is available for cleansing—until the whole of the lime or magnesia in the water has entered into combination with the fatty acids to form the scum of which we have spoken. The hardness of any sample of water is indeed measured by adding a standard soap solution little by little to a known volume of the water until a lather is formed; the more soap solution required to effect this, the harder is the water.

The softening of water.—Carbonate of lime is insoluble in pure water, but readily dissolves in water containing carbon dioxide. Natural waters, especially when they have passed through a layer of peat, become highly charged with carbon dioxide, and if in this condition they come into contact with limestone (this being essentially calcium carbonate) they take up calcium carbonate and are rendered hard.

Exp. 50.—To a few cubic centimetres of lime water add four or five times the volume of distilled water, and pass a stream of carbon dioxide through the clear liquid. At first a turbidity is produced, owing to the formation of calcium carbonate—

$$CaO + CO_2 = CaCO_3.$$

Continue to pass the gas and the liquid will become quite clear again, because we have now carbon dioxide in solution in the water. Divide the clear liquid into two portions, and boil one portion for a little time; to the other add a volume of lime water equal to that originally taken. In each case the turbidity first noticed will be reproduced, since in each case we have got rid of the excess of carbon dioxide; in the first case we expelled the excess of carbon dioxide by heat, in the second we added sufficient lime to combine with it and form calcium carbonate.

We may, then, precipitate the calcium carbonate and get rid of the hardness due to this cause, (*a*) by boiling the water, (*b*) by adding to it the proper amount of lime (Clark's process), and after allowing the precipitate to settle the water will be found to yield a lather with less soap than before: it has become softer. Hardness due to calcium and magnesium carbonates can be removed in this way, and is termed *temporary hardness.* The hardness due to sulphates and chlorides of lime, magnesia, etc., cannot, however, be got rid of by boiling, and is known as *permanent hardness.* Boiling water in a kettle or steam boiler therefore makes it softer, and the "fur" which forms on the vessel is chiefly calcium carbonate which has been precipitated during the process.

SUMMARY.

1. In this chapter, water is treated essentially from a physical point of view:
    - (*a*) as a solid, liquid, or gaseous body;
    - (*b*) as a solvent.
2. *Characteristic properties:*—
    - (*a*) Great capacity for heat, *i. e.* high specific heat.
    - (*b*) Freezes to ice or snow at 0° C.
    - (*c*) Boils (under normal pressure) at 100° C.
3. *Latent heat* of the change from the solid state (ice) to the liquid (water), and of the change from the liquid state to the gaseous (steam).

    Many other solid bodies when they melt or when they are dissolved in water show similar behaviour.

    "Freezing mixtures" owe their low temperature to the absorption of heat during the passage of certain substances from the solid to the liquid state.
4. *Water as a solvent.*

    Specially important is its power of dissolving most gases and solids, some to a slight extent, others readily.

    Solubility of gases decreases with rise of temperature.

    Solubility of gases increases directly as the pressure.

    Solubility of solids usually greater at higher temperatures and pressures.

5. Importance of these facts in connection with natural waters. Note the typical characters of the gases and solids dissolved in rain, river, spring, and sea-waters.
6. Essential characters of drinking water.
   - (*a*) Taste or effect on the palate.
   - (*b*) Freedom from suspended matter.
   - (*c*) „ „ organic matter, especially decaying organic matter.
7. *Hardness of water.*
   - (*a*) *Permanent*, due to dissolved salts, such as sodium chloride, calcium, and magnesium sulphate, etc.
   - (*b*) *Temporary*, due to certain bodies such as calcium and magnesium carbonate, which are practically insoluble in water unless it contains carbon dioxide.

   Note how soap is acted upon by hard and soft water.
8. Pure water has no taste or smell, and except in a very thick layer it is colourless. It should leave no residue on evaporation and give rise to no turbidity or colouration with barium chloride, nitrate of silver or Nessler's reagent.

QUESTIONS.—CHAPTER VIII.

1. Trace the changes in volume that occur when heat is applied to a mass of ice until it melts and passes into vapour.
2. What do you understand by the term "latent heat"? Under what circumstances does heat become latent, and what becomes of the heat thus rendered latent?
3. A is a liquid obtained by mixing together 100 grammes of ice at 0° C. and 100 grammes of boiling water, B is obtained by mixing 100 grammes of water at 0° C. and 100 grammes of boiling water; will the temperature of A differ from that of B? Explain.
4. How many units of heat are required (1) to raise the temperature of 100 grammes of water from 10° C. to 50° C., (2) to just melt 100 grammes of ice?
5. When is a solution said to be *saturated?* What amount of potassium nitrate (see table, p. 82) would be required to form a saturated solution in 150 c.c. of water, (*a*) at zero, (*b*) at 50° C.?
6. What volume of CO_2 will dissolve in 250 c.c. of water under standard pressure, (*a*) at zero, (*b*) at 20° C., and what at these temperatures when the pressure is that of 76 m.m. of mercury, and when it is three atmospheres?
7. In what respects does a typical sample of rain water differ from the water of the Thames?
8. How does it come about that sea water contains more matter in solution than river water?
9. What are the essential qualities of good drinking water?
10. Why is more soap required to produce a permanent lather with *hard* water than with *soft* water?
11. State the constituents to which the temporary and permanent hardness of water are respectively due.
12. Explain the circumstances under which the addition of limewater renders a water soft, and state why it does so.
13. How can calcium carbonate be made to dissolve freely in water, and how may the calcium carbonate be precipitated out of such water again without the addition of chemical reagents?

CHAPTER IX.

OXYGEN AND OXIDES.

OXYGEN, Sulphur, Selenium, and Tellurium all belong to the same chemical family, the resemblance between the last three being of the closest character; but that oxygen and sulphur are allied will be seen from the following statements.

Both elements form allotropic modifications.

Their compounds have a similar chemical composition: this most important fact is illustrated by the following examples:—

The *oxides* of elements have nearly always *sulphides* corresponding to them; *e. g.*—

$$\begin{array}{ccccccc} CO & CO_2 & H_2O & H_2O_2 & K_2O & K_2O_2 & HgO \\ CS & CS_2 & H_2S & H_2S_2 & K_2S & K_2S_2 & HgS. \end{array}$$

The *hydroxides* of elements have *hydrosulphides* corresponding to them:—

$$\begin{array}{ccc} KOH & Ca(OH)_2 & \underset{\text{Alcohol}}{C_2H_5OH} \\ KSH & Ca(SH)_2 & \underset{\text{Mercaptan}}{C_2H_5SH.} \end{array}$$

Some of the *carbonates* have *sulphocarbonates* corresponding to them—

$$\begin{array}{ccc} H_2CO_3 & Na_2CO_3 & K_2CO_3 \\ H_2CS_3 & Na_2CS_3 & K_2CS_3. \end{array}$$

This similarity in composition is also accompanied by a general chemical agreement which is shown in the behaviour of oxysalts and sulphosalts as reagents.

Occurrence.—Although oxygen constitutes about one-half of the whole mass of the earth, it remained unisolated till 1774. This may be attributed to the fact that although it exists in the free state in the atmosphere, the separation from the nitrogen associated with it is not easily accomplished, and to obtain it from mineral substances in which it occurs is even more difficult.

It was first obtained indirectly from air, the oxygen of which was caused to combine with mercury by long-continued heating in contact with air, red oxide of mercury being formed on the surface. Priestley obtained oxygen from this oxide of mercury by heating it to a somewhat higher temperature.

Preparation.—(1) In the laboratory it may be prepared by heating potassium chlorate in a glass flask. The potassium chlorate first fuses, and when the gas begins to come off, the heat should be moderated, otherwise the decomposition takes place too violently. It is found convenient to intimately mix (the potassium chlorate being first powdered in a clean mortar) about one-third the quantity of manganese dioxide with the chlorate, as the decomposition then takes place at a lower temperature and with greater regularity.

$$\underset{\text{Potassium chlorate.}}{2\,KClO_3} = \underset{\text{Potassium chloride.}}{2\,KCl} + 3\,O_2.$$

(2) When it is required in small quantity, it may be obtained by heating mercuric oxide as already mentioned—

$$2\,HgO = 2\,Hg + O_2.$$

(3) Manganese dioxide (the mineral pyrolusite) also yields oxygen when heated; in this case a higher temperature is required, and instead of a glass flask, an iron bottle is used. Only one-third of the oxygen contained by manganese dioxide can be expelled by heat, a lower oxide of manganese being left behind—

$$3\,MnO_2 = Mn_3O_4 + O_2.$$

Some other oxides give up oxygen when heated, *e.g.*—

$$3\,PbO_2 = Pb_3O_4 + O_2.$$
$$4\,CrO_3 = 2\,Cr_2O_3 + 3\,O_2.$$
$$2\,BaO_2 = 2\,BaO + O_2.$$
$$2\,Ag_2O = 4\,Ag + O_2.$$

Oxygen is also evolved when certain salts (such as potassium permanganate, $KMnO_4$), rich in oxygen, are decomposed by heat or by the action of strong acids. Peroxides when heated with sulphuric acid also evolve oxygen, *e.g.*—

$$2\ MnO_2 + 2\ H_2SO_4 = 2\ MnSO_4 + 2\ H_2O + O_2.$$

This method was first used by Scheele, who discovered oxygen independently of Priestley.

In recent years oxygen has been obtained on the large scale indirectly from air by means of baryta, BaO (Brin's process). When this body is heated to *dull redness* in air it takes up oxygen and is converted into the dioxide—

$$2\ BaO + O_2 = 2\ BaO_2.$$

This dioxide at a *bright red heat* gives up the oxygen which it had taken up, and is transformed again into baryta—

$$2\ BaO_2 = 2\ BaO + O_2.$$

By alternately heating to the lower and the higher limit of temperature oxygen is successively taken from the air and given up again, so that the same charge of baryta may be the means of furnishing an indefinitely large quantity of oxygen. In practice the same result is achieved by keeping the temperature constant and varying the pressure, air free from moisture and carbon dioxide being passed over the oxide at a pressure of two atmospheres. When the baryta has been converted into barium dioxide, if the retort containing it be exhausted so as to diminish the pressure, it is no longer necessary to apply a bright red heat to drive off the oxygen, since the decomposition of the higher oxide at the low pressure also takes place at the same temperature as is required for the formation of the dioxide.

Properties of oxygen.—Oxygen possesses no odour, it is colourless, and only slightly soluble in water, which at ordinary temperatures absorbs about $\frac{1}{30}$ of its volume of the gas.

Pictet found that it required a pressure of over 100 atmospheres at − 140° C. to liquefy oxygen. The liquid oxygen is strongly magnetic; in its chemical properties it is much less active than in the gaseous condition, being without action even on phosphorus.

The distinguishing feature of oxygen is that it combines readily with nearly all the elements, and often with such energy that the union is accompanied by manifestation of light and heat. This phenomenon is termed "combustion," and oxygen is consequently a *powerful supporter of combustion.* A glowing splinter of wood, if plunged into oxygen, immediately bursts into flame, a property which is only shown by one other gas, nitrous oxide. The following experiments illustrate the properties of oxygen—

Exp. 51.—A small piece of sulphur is placed on a deflagrating spoon and ignited, it is then plunged into a jar of oxygen. The flame is seen to be much brighter than in air, and there is produced a suffocating gas known as sulphur dioxide, SO_2. On afterwards pouring water into the jar and shaking it up, this gas dissolves and forms a solution of sulphurous acid, H_2SO_3. The acid character of the solution is shown by its turning blue litmus red.

$$S + O_2 = SO_2, \text{ and } SO_2 + H_2O = H_2SO_3.$$

Exp. 52.—A piece of ordinary phosphorus[1] the size of a pea is ignited in a deflagrating spoon and brought into a jar of oxygen. A very vivid combustion ensues, the phosphorus combining with oxygen to form phosphorus pentoxide, P_2O_5, a very finely-divided white solid which dissolves very readily in water, forming metaphosphoric acid, HPO_3.

$$4\ P + 5\ O_2 = 2\ P_2O_5, \text{ and } P_2O_5 + H_2O = 2\ HPO_3.$$

Exp. 53.—Charcoal (carbon) glows and scintillates very brightly in oxygen, forming carbon dioxide, CO_2. This, when shaken up with water, dissolves, the liquid showing a feebly acid reaction, so that the litmus is changed to a wine-red colour as distinguished from the bright red shown by stronger acids.

$$C + O_2 = CO_2, \text{ and } CO_2 + H_2O = H_2CO_3.$$

But such examples of combination with the evolution of light and heat are not confined to non-metals, for many of the metals, especially in the finely-divided condition, show vivid combustion.

Exp. 54.—A few strands of fine iron wire are twisted loosely together, ignited,[2] and then introduced into oxygen. The wire burns with bright scintillations, forming an oxide of iron, Fe_3O_4, which falls in globules to the bottom of the vessel. It is insoluble in water.

$$3\ Fe + 2\ O_2 = Fe_3O_4.$$

---

[1] Great care must be exercised in handling phosphorus, as it ignites with the warmth of the hand; it should be cut under water, and rapidly dried between filter paper.

[2] The combustion may be started by tying a small piece of string or hemp to the end of the wire and igniting this in the flame of a Bunsen burner previously; also it is well to put a layer of sand in the bottom of the cylinder to prevent breakage.

Similarly, sodium burns brightly in oxygen, forming the oxide Na_2O_2.

Such experiments afford very striking illustrations of the energy with which oxygen enters into combination with many elements, but it must not be overlooked that even at ordinary temperatures the process of oxidation goes on, though more slowly. Thus the freshly-cut surface of sodium is quite bright and silvery, but very rapidly tarnishes, owing to the formation of a film of oxide. Iron rusts in moist air, and lead loses its bright metallic surface and gradually tarnishes. Phosphorus fumes and gives out a faint luminosity in air forming phosphorous oxide, P_4O_6. Organic matter and some mineral substances, such as iron pyrites, also undergo oxidation in the air at ordinary temperatures; and finally, oxygen plays an important part in vital processes, both in the animal and vegetable organism, transforming carbonaceous matters ultimately into carbon dioxide, and hydrogenous substances into water.

The oxides.—With the exception of fluorine and bromine, all the elements form, with oxygen, compounds called the oxides.

The oxides of the alkali metals—soda, Na_2O, potash, K_2O—readily combine with water, forming *hydroxides*, $NaOH$, KOH, and those of the alkaline earths, lime, CaO, strontia, SrO, baryta, BaO, likewise form hydroxides, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$. They are soluble in water, and the solution has caustic properties, a soapy feel, and turns red litmus blue. A substance which turns red litmus blue is indeed said to have *an alkaline reaction* to litmus. Such oxides are known as *basic oxides* or *bases*.

On the other hand, the oxides of the non-metallic elements, SO_2, SO_3, CO_2, P_2O_5, N_2O_5, B_2O_3, etc., combine with water, forming acids, H_2SO_3, H_2SO_4, H_2CO_3, HPO_3, HNO_3, H_3BO_3, etc., and these are often corrosive, possess a sour (acid) taste, and turn blue litmus red.

So far, then, as these oxides are concerned we have two classes of oxides, differing in the properties enumerated. Let us now see what happens when we bring together members of each of these classes.

Exp. 55.—Take about 25 c.c. of a solution of caustic potash, KOH, add a little litmus to it, which will become blue; now add nitric acid (HNO_3) little by little, until the last drop just gives a wine-red tint to the liquid. In this condition the liquid is said to have *a neutral reaction* to litmus paper, and the addition of a single drop of the alkali will turn it *blue*, whilst the addition of a single drop of an acid will turn it *red*. Now evaporate the solution down until, on cooling and standing a little while, a clear colourless solid separates out.

Neither caustic potash nor the nitric acid on concentration show any inclination to crystallize, and the solid which is produced differs from the materials from which it has been formed not only in this respect, but also in that when dissolved it has neither an alkaline nor acid reaction, but is neutral. Moreover, heat will be found to have been evolved by the addition of nitric acid to the caustic potash. A chemical combination has been effected between the oxides, and a *salt* has been formed—

Alkaline hydroxide. Acid. Salt.

$$KOH + HNO_3 = KNO_3 + H_2O.$$

Potash. Nitric acid. Potassium nitrate.

A similar experiment may be performed, using sulphuric or hydrochloric acid, the sulphate or chloride of potassium being then formed.

But many oxides which react with acid oxides are insoluble in water, and show no marked caustic properties, nor do they act on litmus; examples of these are zinc oxide, ZnO, lead oxide, PbO, cupric oxide, CuO. They however dissolve in acids in definite quantities, partially or entirely neutralizing the acid, and on evaporating, a salt is obtained, as in the previous case.

Exp. 56.—Digest 5 grammes of zinc oxide with 25 c.c. of dilute sulphuric acid (see footnote, p. 29) on a water-bath for some minutes; some of the zinc oxide will remain undissolved, as we have taken a larger quantity than suffices to combine with the whole of the sulphuric acid. Now filter or decant off the clear liquid and concentrate it, until on cooling and standing crystals separate out. This is a neutral salt, zinc sulphate—

Oxide. Acid. Salt.

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O.$$

Zinc oxide. Sulphuric acid. Zinc sulphate.

Similarly if lime, (CaO) cupric oxide, (CuO) or lead oxide, (PbO)

be digested with sulphuric acid the *sulphates* of lime, copper and lead will respectively be obtained and water eliminated:—

$$CaO + H_2SO_4 = CaSO_4 + H_2O.$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$
$$PbO + H_2SO_4 = PbSO_4 + H_2O.$$

If nitric acid be used, the corresponding *nitrates* are obtained:—

$$ZnO + 2\ HNO_3 = Zn(NO_3)_2 + H_2O.$$
$$CaO + 2\ HNO_3 = Ca(NO_3)_2 + H_2O.$$
$$CuO + 2\ HNO_3 = Cu(NO_3)_2 + H_2O.$$
$$PbO + 2\ HNO_3 = Pb(NO_3)_2 + H_2O.$$

If hydrochloric acid be used, the *chlorides* are obtained:—

$$ZnO + 2\ HCl = ZnCl_2 + H_2O.$$
$$CaO + 2\ HCl = CaCl_2 + H_2O.$$
$$CuO + 2\ HCl = CuCl_2 + H_2O.$$
$$PbO + 2\ HCl = PbCl_2 + H_2O.$$

All oxides or hydroxides which enter into combination with acids to form salts, whether (like potash) they have an alkaline reaction or no such reaction (like zinc oxide), are termed *basic oxides.* And *salts* are bodies formed by the combination of basic oxides or hydroxides, termed *bases*, with acid oxides or hydroxides, termed more generally *acids.* Salts can generally be obtained in a crystalline form, and though usually neutral in their reaction, may show an acid or alkaline reaction. Sodium carbonate, for instance, is a salt with an alkaline reaction, whilst ferric sulphate has an acid reaction.

Tests for Oxides.—(1) The oxides may generally be distinguished from the metals by the absence of lustre, and by the fact that when dissolved in acids no hydrogen is evolved—

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O.$$

(2) Many oxides give up oxygen when heated strongly (see p. 92), or give rise to the formation of water when heated in a current of hydrogen, or when mixed with carbon, part or the whole of the oxygen uniting with hydrogen or carbon.

$$CuO + H_2 = Cu + H_2O.$$

(3) Oxides not decomposed when heated in hydrogen, or with carbon alone (*e. g.* silica), may usually be shown to contain oxygen by mixing with finely divided carbon and heating in a stream of chlorine, when carbon monoxide is obtained.

SUMMARY.

Oxygen.

1. *Preparation.*
    - (*a*) From potassium chlorate.
    - (*b*) From HgO, Ag_2O, MnO_2, BaO_2, and some other oxides.
    - (*c*) From $KMnO_4$, or peroxides by the action of H_2SO_4.
2. *Properties.*
    - (*a*) Slightly soluble in water.
    - (*b*) Combustion of S, P, C, Fe, Na, etc. in oxygen.
    - (*c*) Oxidation at ordinary temperatures is usually a slow process—*e. g.* sodium tarnishing, iron rusting, phosphorus fuming, C and H in organisms; sometimes it takes place more rapidly, *e. g.* finely divided P, Fe, Pb, etc.
3. *The oxides and hydroxides.*
    - (*a*) Basic oxides (Na_2O, CaO, etc.) which unite with water forming hydroxides ($NaOH$, $Ca(OH)_2$, etc.), those soluble in water having an *alkaline* reaction to litmus.
    - (*b*) Acidic oxides (SO_3, N_2O_5, etc.) which unite with water forming hydrogen salts or acids—(H_2SO_4, HNO_3, etc.)—those soluble in water having an *acid* reaction to litmus.
    - (*c*) Salts sometimes formed by bringing together basic oxides and acidic oxides, *e. g.*

$$CaO + SO_3 = CaSO_4$$

or by the action of basic oxides, or hydroxides on hydrogen salts or acids, *e. g.*

$$CaO + H_2SO_4 = CaSO_4 + H_2O.$$
$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2\ H_2O.$$

and similarly with Na_2O, CuO, PbO, ZnO, etc.

4. *Characters of oxides.*
    - (*a*) Usually amorphous powders.
    - (*b*) When dissolved in acids no hydrogen is evolved (as when elements react with acids), but water is formed.
    - (*c*) Some oxides (HgO, Ag_2O) give up oxygen when they are merely heated.

      Many oxides (CuO, PbO, etc.) give up oxygen when heated in presence of carbon or hydrogen.

      Some (SiO_2, CaO, Al_2O_3, etc.) are unchanged even when heated in presence of carbon or hydrogen.

QUESTIONS.—CHAPTER IX.

1. How was oxygen first isolated? Mention any oxides which will give up oxygen when they are heated.
2. State how baryta may be used as a means of obtaining oxygen from the atmosphere.
3. How is oxygen usually prepared in the laboratory?
4. What are the characteristic properties of gaseous oxygen, and in what respects do they differ from those of liquid oxygen?
5. Give instances of the formation of oxides by the action of oxygen on elementary substances, (*a*) where such action takes place at ordinary temperatures, (*b*) where heat must be applied in order to start the reaction.
6. What takes place when the products of combustion of carbon, sulphur, phosphorus, and sodium are respectively brought into contact with water?
7. What is an *oxide?* Give instances of oxides of the metals which are soluble in water, and of oxides which are insoluble in water.
8. How do acid-forming oxides (anhydrides) differ from basic oxides? What is usually the effect of bringing together solutions of these two classes of oxides?
9. Given metallic magnesium and sulphuric acid, how would you prepare a specimen of Epsom salt ($MgSO_4 . 7 H_2O$)?
10. What experiments would you perform in order to show that (*a*) oxide of lead, (*b*) oxide of copper, and (*c*) silica contain oxygen?

CHAPTER X.

THE EQUIVALENT—NOMENCLATURE.

The equivalent.—The *atomic weight* of an element is the smallest weight (in relation to hydrogen as unity) of the element which enters into the composition of a molecule of any of its compounds. *The equivalent is the relative weight of an element which replaces one part of weight of hydrogen.*[1]

Methods of determining the equivalent.

For those metals which act upon dilute acids evolving hydrogen it is only necessary to determine

(*a*) the amount of metal dissolved;

(*b*) ,, ,, ,, hydrogen given off during the reaction.

The following experiments will show how this may be done.

(1) **Determination of weight of hydrogen evolved.**

Exp. 57.—A wide-mouthed weighing bottle of thin glass is fitted with a rubber stopper and tubes, as shown in the figure, and about 5 c.c. of water run into it. One of the tubes is simply bent at right angles, and closed with a short piece of rubber tubing and glass rod. The other is furnished with a bulb lightly packed with dry fibrous asbestos or glass wool, and concentrated sulphuric acid is introduced into its lower part, as shown, by dipping it up to its orifice, in a test tube containing the acid.[2] The outside is then rinsed with water (from a wash bottle), so as to remove any acid adhering to it. A quantity of magnesium (not more than 0·2 gramme) is accurately weighed and dropped into the bottle, and the india-rubber cork fitted into its place. The whole apparatus is then weighed.

---

[1] In some cases, notably with the non-metals, the direct replacement of hydrogen in hydrogen salts cannot be effected, and the equivalents for them are the relative weights which enter into combination with one part by weight of hydrogen in the formation of such compounds as H_2O, HCl, H_2S, H_3N, etc.

[2] The tube should be of such dimensions as to hold at least 2 c.c. of the acid.

Momentarily removing the glass rod, blow gently down the bulb tube till about half the acid is expelled, and quickly replace the glass rod. The acid is acted upon by the metal, hydrogen is evolved and passes out by the only exit left for it, viz. the bulb tube ; the concentrated acid still remaining there serves to dry the gas. When the metal is all dissolved, remove the glass rod and draw a gentle current of air through the apparatus, so as to replace any hydrogen in the bottle, replace the rod, and again weigh. A decrease of weight will be found to have occurred owing to the hydrogen discharged from the apparatus, *e. g.*

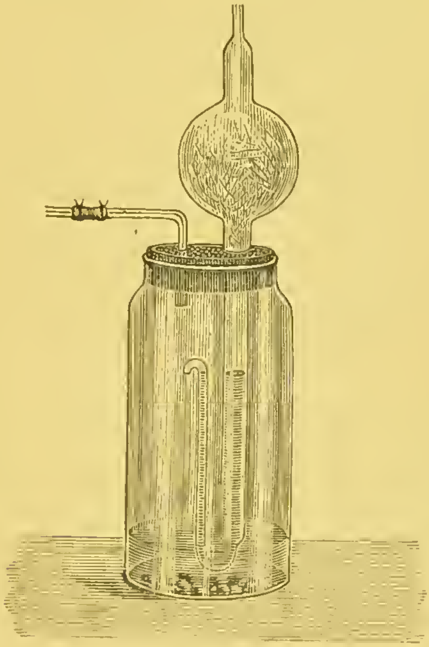

FIG. 18.

Weight of apparatus	before	reaction	35·534	grammes.
,, ,,	after	,,	36·520	,,
	Loss of weight		0·014	,,

This is the weight of the hydrogen evolved. The weight of magnesium taken was 0·168 gramme. The equivalent of magnesium is then—

$$\frac{0{\cdot}168}{0{\cdot}014} = 12.^{1}$$

Similarly other metals such as iron, zinc, and aluminium may be used in place of magnesium, and the equivalents should be found to agree fairly accurately with the numbers 28, 32·5, and 9 respectively. The equations representing the reactions are :—

$$\begin{aligned} Mg + H_2SO_4 &= MgSO_4 + H_2. \\ Fe + H_2SO_4 &= FeSO_4 + H_2. \\ Zn + H_2SO_4 &= ZnSO_4 + H_2. \\ 2\,Al + 3\,H_2SO_4 &= Al_2(SO_4)_3 + 3\,H_2. \end{aligned}$$

(2) **Determination of volume of hydrogen evolved.**

More frequently in practice the volume of the hydrogen evolved is measured, and its weight calculated from this.

Several methods have been suggested for determining the volume of the hydrogen which are sufficiently accurate for the purpose. A very simple one is described in the following experiment.

Exp. 58.—Take a Cowper's tube, with stopper, as shown in the figure, and of at least 100 c.c. content. Remove the stopper, close the lower opening with the finger, and pour in about 50 c.c. of dilute hydrochloric acid; fill up with a gentle stream of water, so that it mixes as little as possible with the acid. Now introduce at the stoppered end about (the weight being previously correctly ascertained) 0·05 gramme of magnesium ribbon tightly rolled up into a small compass, insert the stopper *at once.* As soon as the magnesium comes into contact with the acid, hydrogen is evolved. When the whole of the metal is dissolved, mark the level of the water in the tube, previously sinking the tube in water to the level of the liquid within it, and measure the volume of the gas.[2]

---

[1] This elegant method of directly determining the weight of hydrogen evolved by a given weight of a metal is taken from Prof. Tilden's *Hints on the Teaching of Elementary Chemistry*, and the figure is reproduced here by permission of Messrs. Longmans, Green and Co.

[2] To do this, if the tube is not graduated, remove the stopper, close the lower opening with the finger, and note the amount of water required to just fill the tube again up to the level of the stopper.

The equation representing the reaction is—

$$Mg + 2\,HCl = MgCl_2 + H_2.$$

It is evident that before the weight of hydrogen evolved can be determined allowance must be made for—

(*a*) the temperature of the gas (the room):
(*b*) the pressure to which it is subjected (that of the atmosphere at the time of the experiment);
(*c*) the tension of water vapour.

This involves a somewhat complex calculation, and a table has therefore been prepared by which the weight of the hydrogen may be readily arrived at. (See Appendix, p. 203.)

Exp. 59.—Perform a similar experiment with aluminium foil, about 0·04 gramme; the evolution of gas takes place much more slowly[1] than in the case of the magnesium, and the whole tube may be filled with dilute hydrochloric acid, since the action does not commence immediately. Zinc or iron wire may also be used for determinations, taking in each case about 0·1 gramme of the metal.

The gas must not of course be allowed to issue at the lower orifice of the Cowper's tube, and with a little tact any loss here may be readily avoided.

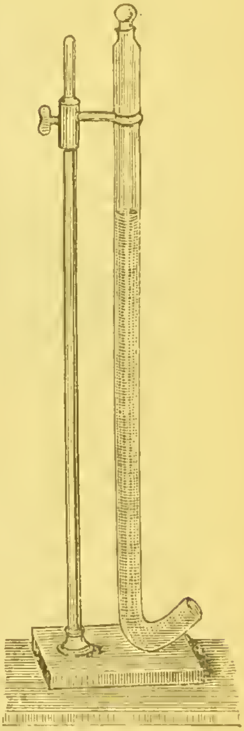

FIG. 19.

The equations for the reactions are—

$$2\,Al + 6\,HCl = Al_2Cl_6 + 3\,H_2.$$
$$Zn + 2\,HCl = ZnCl_2 + H_2.$$
$$Fe + 2\,HCl = FeCl_2 + H_2.$$

The estimation of the equivalent of the alkali metals, K, Na &c., offers some difficulty, owing to the violence of the reaction and the rapidity with which these metals are acted upon when exposed to air. This may, however, be overcome by using an amalgam of the metal prepared in the following manner.[2]

---

[1] Warm solution of caustic soda or potash may with advantage be substituted for the acid.

[2] This experiment should be made by the teacher, at any rate it should not be performed by a beginner.

Weigh a small specimen tube and cork, then quickly introduce a piece of sodium (handled with *dry* fingers) about the size of a pea; cork the tube and weigh again, hence obtaining the weight of the piece of sodium. Now take about 10 c.c. of dry warm quicksilver in a small mortar, drop the sodium out of the tube on the surface of this, and press it firmly beneath the mercury with the pestle against the bottom of the mortar. The sodium will associate with the mercury to form *sodium amalgam*, and some heat will be evolved. Now bring the whole of the amalgam into a porcelain crucible, and place this in a vessel of water and under the mouth of an inverted cylinder filled with water. Hydrogen will instantly commence to rise from the surface of the amalgam and collect in the cylinder. The volume of the gas must be measured and its weight determined, as in previous experiments.

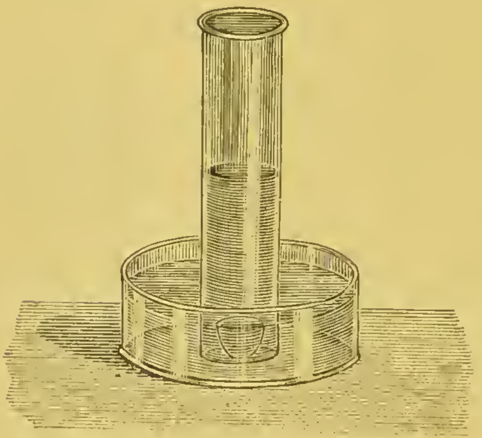

FIG. 19*a*.

We have then weight of sodium $= W$

" " hydrogen $= w$

Equivalent of sodium $= \frac{W}{w}$.

A striking method of determining the equivalent may also be shown by passing hydrochloric acid gas over sodium gently heated in a tube and collecting the hydrogen evolved, but this also should not be attempted by the student except under careful supervision by the teacher.

(3) **Determination by deposition of metal.**

Another method by which the equivalent may be determined is applicable in some cases where the foregoing cannot be used. This is the deposition of a metal from a solution of one of its salts by placing in it a more electropositive metal. For instance, if metallic magnesium, or zinc, or iron be introduced into a solution of silver nitrate or copper sulphate, etc., finely divided silver or copper will be thrown down, and the amounts deposited under like conditions are proportional to the equivalents of the metals in question. The reaction which takes place is—

$$\begin{aligned} CuSO_4 + Mg &= Cu + MgSO_4. \\ 2\,AgNO_3 + Mg &= 2\,Ag + Mg(NO_3)_2. \\ CuSO_4 + Fe &= Cu + FeSO_4. \\ 2\,AgNO_3 + Zn &= 2\,Ag + Zn(NO_3)_2. \end{aligned}$$

Exp. 60.—Weigh accurately a rather deep porcelain crucible of about 50 c.c. content. Into this bring about 40 c.c. of a solution containing not less than 2 grammes of copper sulphate, and then about 0·15 gramme of magnesium ribbon, the exact weight of which has been determined. The magnesium will slowly disappear, and a heavy powder will be precipitated to the bottom of the vessel. When on stirring with a glass rod there is no longer any sign of the foil, the reaction is complete. The magnesium has replaced the copper in the salt originally taken, and we have now in the vessel metallic copper and a solution containing magnesium sulphate and excess of copper sulphate. Now place the porcelain crucible in the centre of a basin of about the same

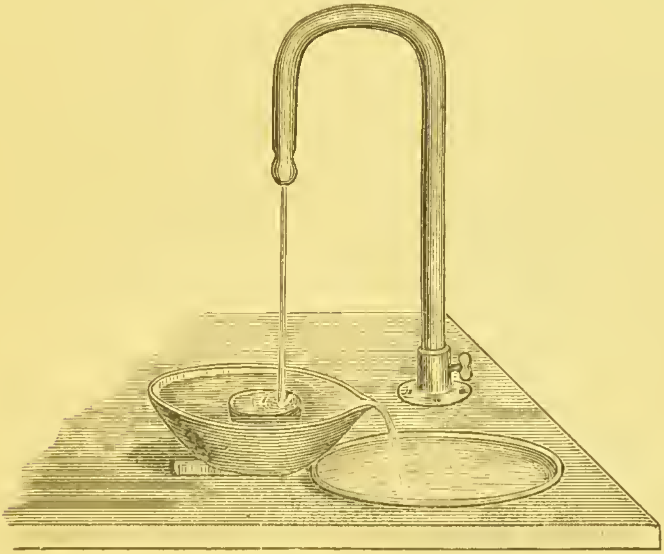

Fig. 20.

depth, and direct a *very gentle* stream of water on the surface of the liquid, as shown in the figure. Adjust the stream so that little if any of the particles are so disturbed as to be carried out of the crucible, and allow it to continue some minutes and so long as the faintest trace of blue colour[1] is to be seen. Now take out the crucible, pour off the liquid carefully, so as to avoid the loss of any copper, and if some granules are found at the bottom of the basin, pour off the liquid in it and wash these into the crucible. After the water has been drained away as completely as possible from the copper, add a few cubic centimetres of alcohol, pour off again and repeat this washing with alcohol once or twice more. Now place the crucible in a desiccator, allow it to remain till quite dry, and then weigh it. The increase in weight will represent the amount of copper it contains.

We have now (*a*) the weight of magnesium used, (*b*) the equivalent weight of copper which this magnesium has displaced, and if the experiment has been carried out with due care these weights will be found to show very nearly the relation 12 : 31·6. Thus if 12 be accepted as the equivalent of magnesium, 31·6 must be taken as that of copper. Similarly if a solution of nitrate of silver be substituted for that of copper sulphate, the equivalent of silver may be determined. An experiment of the same kind may be performed with metallic iron and copper sulphate.

Quite analogous to this is the deposition of metals which occurs during the electrolysis of solutions of their salts. We have already seen (p. 71) that when water is decomposed we obtain two volumes of hydrogen for one of oxygen, or 8 parts by weight of oxygen are united to 1 part by weight of hydrogen. Supposing now we were to introduce the platinum electrodes into a weak aqueous solution of sulphate of copper, there would be copper deposited on the electrode, at which in the former experiment hydrogen had appeared. Similarly with sulphate of silver solution we should have silver deposited. Further than this, ascertain the weight of the hydrogen evolved in a given time, and compare this with the weight of copper, silver, etc., deposited in the same time as determined by weighing the platinum before and after the deposition.[1]

---

[1] On adding ammonia to a little of the liquid in a test-tube the blue colour is intensified, and, if then on looking down the tube the colour is no longer apparent, the washing may be discontinued.

Taking hydrogen as unity, we shall have as the

Equivalent of oxygen (from electrolysis of water) = 8
,, copper (,, ,, $CuSO_4$) = 31·6
,, silver (,, ,, Ag_2SO_4) = 108·0

and similarly with other elements.

(4) **Determination by reduction of oxide.**

Again, the equivalent may be determined by ascertaining the weight of hydrogen required to produce a certain weight of metal by reduction of its oxide. This method can only be used in the case of those oxides which are readily reducible in hydrogen, such as the oxides of copper, iron, lead, etc.

Exp. 61. A glass tube about 15 m.m. wide and 20 c.m. long is drawn out in the form shown below, and about 2 grammes of finely powdered black oxide of copper[2] are introduced into it in an even layer, or better, in a porcelain boat. At the wider end it is fitted with a cork, and attached to a U tube containing granular calcium chloride. The drawn out end is attached to a supply of hydrogen dried by being passed over calcium chloride in a U tube. The hydrogen should be allowed to pass for two

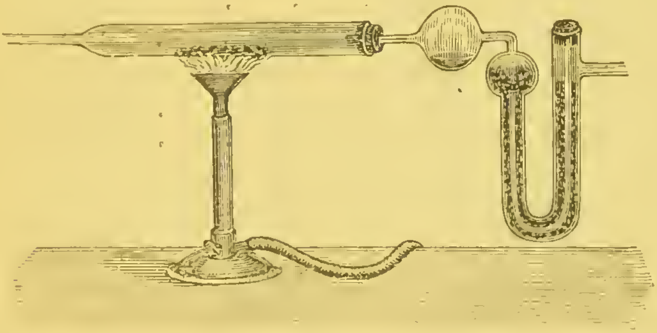

FIG. 21.

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[1] It is assumed that the current from the battery is the same in each experiment; this may be best secured by connecting up the water voltameter and the solutions of copper, silver, etc. in series, so that the same current passes through each of them.

[2] This should be previously heated to redness in air (to get rid of moisture, etc. attached to it), and, whilst still warm, introduced into the tube just before commencing the experiment.

or three minutes before heat is applied, in order to displace the air in the tubes, or an explosion may occur. On heating the oxide of copper it will slowly change to a dark red, and water will be seen to condense in the further end of the tube and the bulb of the U tube. The heating must be continued and the stream of hydrogen passed until no more traces of moisture are observed in the straight tube, and care must be exercised to prevent the further end of the tube becoming so hot as to affect the cork. Most of the moisture will now collect in the bulb of the U tube, and the rest will be absorbed by calcium chloride. The details below, from an actual experiment, will show the weighings to be made, and the method by which the equivalent may be deduced.

Weight of heating tube alone . . .	38·26	grammes.
„ „ „ and copper, taken after heating is finished and tube has been allowed to cool	39·74	„
Hence weight of copper remaining . .	1·48	„
Weight of U tube before experiment .	16·57	„
„ „ after „ . .	16·99	„
Hence weight of water formed . . .	0·42	„
and „ „ hydrogen which has taken part in the reaction is one-ninth (see page 72) of this	0·047	„
Equivalent of copper $= \frac{1·48}{0·047} =$	31·5	„

Similarly litharge (oxide of lead) PbO, or ferric oxide, Fe_2O_3, may be used, and we have—

$CuO + H_2 = Cu + H_2O$ equivalent of Cu = 31·6
$PbO + H_2 = Pb + H_2O$ „ „ Pb = 103·5
$Fe_2O_3 + 3\,H_2 = 2\,Fe + 3\,H_2O$ „ „ Fe = 18·7

Some metals form two or more oxides; for instance, in addition to the ferric oxide, Fe_2O_3, already mentioned, there is the lower oxide (ferrous oxide), FeO, and the magnetic oxide, Fe_3O_4. These when heated in hydrogen undergo reduction in accordance with the equations—

$FeO + H_2 = Fe + H_2O$ equivalent = 28·0
$Fe_3O_4 + 4\,H_2 = 3\,Fe + 4\,H_2O$ „ = 21·0

The red oxide of copper (cuprous oxide), Cu_2O, affords another instance of the same kind—

$$Cu_2O + H_2 = 2\ Cu + H_2O \text{ equivalent } = 63{\cdot}2$$

Finally, those metals which have two or more oxides frequently form more than one series of salts, and these regarded as resulting from the replacement of hydrogen in the hydrogen salts (acids) likewise show equivalents of different values, thus—

$FeSO_4$	from	**H_2SO_4**	equivalent	28·0,	as in	FeO.
$Fe_2(SO_4)_3$	„	**3 H_2SO_4**	„	18·7,	„	Fe_2O_3.
HgCl	„	**HCl**	„	200,	„	Hg_2O.
$HgCl_2$	„	**2 HCl**	„	100,	„	HgO.
CuCl	„	**HCl**	„	63·2,	„	Cu_2O.
$CuCl_2$	„	**2 HCl**	„	31·6,	„	CuO.

The composition of water being represented by the formula H_2O indicates that the equivalent of oxygen is 8, and by using this factor the equivalents of the element deduced from its oxides will correspond to that obtained in the previous paragraph.

Thus the proportions in which the elements iron, mercury, and copper unite with oxygen to form different oxides is as given below, and the equivalents deduced will be found to agree with those already stated.

						Equivalent of element.	Equivalent of oxygen.
In FeO	weight of Fe	: that of O	:: 56	: 16	or	28	: 8
„ Fe_3O_4	„ „	: „	:: 168	: 64	„	21	: 8
„ Fe_2O_3	„ „	: „	:: 112	: 48	„	18·7	: 8
„ Hg_2O	„ Hg	: „	:: 400	: 16	„	200	: 8
„ HgO	„ „	: „	:: 200	: 16	„	100	: 8
„ Cu_2O	„ Cu	: „	:: 126·4	: 16	„	63·2	: 8
„ CuO	„ „	: „	:: 63 2	: 16	„	31·6	: 8

and so on in the case of other elements.

In the following table a statement is given of the equivalents and atomic weights of a number of elements, and some of the compounds which exhibit the equivalent relation—

Element.	Atomic weight.	Equivalent.	Oxide.	Chloride.	Sulphate.	Relation atomic weight : Equivalent.
Sodium	23	23	Na_2O	$NaCl$	Na_2SO_4	1 : 1
Potassium	39	39	K_2O	KCl	K_2SO_4	1 : 1
Silver	108	108	Ag_2O	$AgCl$	Ag_2SO_4	1 : 1
Copper	63·2	63·2	Cu_2O	$CuCl$	—	1 : 1
,,	,,	31·6	CuO	$CuCl_2$	$CuSO_4$	2 : 1
Mercury	200	200	Hg_2O	$HgCl$	Hg_2SO_4	1 : 1
,,	,,	100	HgO	$HgCl_2$	$HgSO_4$	2 : 1
Magnesium	24	12	MgO	$MgCl_2$	$MgSO_4$	2 : 1
Calcium	40	20	CaO	$CaCl_2$	$CaSO_4$	2 : 1
Zinc	65	32·5	ZnO	$ZnCl_2$	$ZnSO_4$	2 : 1
Lead	207	103·5	PbO	$PbCl_2$	$PbSO_4$	2 : 1
Iron	56	28	FeO	$FeCl_2$	$FeSO_4$	2 : 1
,,	,,	18·6	Fe_2O_3	Fe_2Cl_6	$Fe_2(SO_4)_3$	3 : 1
Aluminium	27	9	Al_2O_3	Al_2Cl_6	$Al_2(SO_4)_3$	3 : 1
Sulphur	32	8	SO_2	SCl_4	—	4 : 1
,,	,,	5·3	SO_3	—	—	6 : 1
Carbon	12	3	CO_2	CCl_4	—	4 : 1
Tin	119	29·7	SnO_2	$SnCl_4$	$Sn(SO_4)_2$	4 : 1

Nomenclature.—The name applied to a chemical compound is intended as a rule to indicate—

(*a*) the elements of which it is composed;
(*b*) the proportions in which the elements occur;
(*c*) in some cases, its chemical nature as a member of a class.

Thus MnO_2 is manganese *di*oxide,
SO_3 ,, sulphur *tri*oxide,
N_2O_4 ,, nitrogen *tetr*oxide,
NH_3 ,, nitrogen *tri*hydride or ammonia,
HCl ,, hydrogen chloride or hydrochloric acid.

Compounds consisting of only two elements are termed *binary compounds*, and are designated by the termination *ide*, as in the examples quoted above. Where the same elements combine in two different proportions, it is necessary to name them in such a way that they may not be confused with one another. Thus we have seen that mercury and iodine combine with one another to form a green iodide and a red iodide, the former containing for the same amount of mercury only half as much iodine as the latter. In such cases the terminations *ous* and *ic* are applied, *ous* where the proportion of the electronegative element is the smaller.

HgI is therefore called mercur*ous* iodide;
HgI_2 is called mercur*ic* iodide.

Similarly—

Cu_2O is cupr*ous* oxide,
CuO is cupr*ic* oxide,
N_2O is nitr*ous* oxide,
NO is nitr*ic* oxide,
FeO is ferr*ous* oxide,
Fe_2O_3 is ferr*ic* oxide (or sesquioxide of iron).

There are also certain terms applied to *classes* of compounds in consideration of their showing certain definite chemical characters. Thus if we regard salts as composed of a *base* and an *acid*, each being oxides, the basic part is known as the *basic oxide*, and the acid part as the *acid oxide* or *anhydride*.

Potassium sulphate, K_2SO_4, in this sense may be regarded as consisting of the basic oxide K_2O, combined with the acid oxide, SO_3.

			Basic oxide.		Acid oxide.
So copper nitrate,	$Cu(NO_3)_2$,	will be	CuO	.	N_2O_5.
calcium carbonate,	$CaCO_3$,	,,	CaO	.	CO_2.
sodium sulphite,	Na_2SO_3,	,,	Na_2O	.	SO_2.
,, sulphate,	Na_2SO_4,	,,	Na_2O	.	SO_3.

The basic oxide in combination with water forms the *hydroxide*, e. g.

$Ca(OH)_2$ or $CaO.H_2O$.
$Ba(OH)_2$,, $BaO.H_2O$.
$Fe_2(OH)_6$,, $Fe_2O_3.3\,H_2O$.
$2\,NaOH$,, $Na_2O.H_2O$.

The acid oxide where it combines with water forming an acid is termed an *anhydride*.

SO_2	sulphurous	anhydride	H_2SO_3	sulphurous	acid.
SO_3	sulphuric	,,	H_2SO_4	sulphuric	,,
N_2O_3	nitrous	,,	HNO_2	nitrous	,,
N_2O_5	nitric	,,	HNO_3	nitric	,,

It will be observed that the terms *ous* and *ic* are applied to all such compounds, in the same sense as already stated, where it is necessary to adopt a means of distinction. It must be pointed out that where an element forms two series of salts these likewise are similarly designated—

$FeSO_4$	ferr*ous*	sulphate.
$Fe_2(SO_4)_3$	ferr*ic*	,,
$HgNO_3$	mercur*ous*	nitrate.
$Hg(NO_3)_2$	mercur*ic*	,,

Finally those salts derived from the lower acids, bearing the termination *ous*, have the termination *ite*, and those derived from the *ic* acids, the termination *ate*.

H_2SO_3	sulphur*ous*	acid	Na_2SO_3	sodium	sulph*ite*.
H_2SO_4	sulphur*ic*	,,	Na_2SO_4	,,	sulph*ate*.
HNO_2	nitr*ous*	,,	KNO_2	potassium	nitr*ite*.
HNO_3	nitr*ic*	,,	KNO_3	,,	nitr*ate*.

The student must be prepared to find that, in many cases, names are applied to compounds which do not conform to these rules. Thus CO is very frequently and indeed usually called *carbonic oxide*, and CO_2, *carbonic acid gas;* also many common substances are known by names which were given to them before any definite scheme of nomenclature had been adopted. These names are in many cases descriptive of the general appearance or character of the body, and bear little or no relation to its chemical nature. A few instances of such names will be instructive.

Sulphuric acid (H_2SO_4)	is often called	*oil* of vitriol.
Copper sulphate ($CuSO_4.5\ H_2O$)	,,	blue vitriol.
Zinc sulphate ($ZnSO_4.7\ H_2O$)	,,	white vitriol.
Ferrous sulphate ($FeSO_4.7\ H_2O$)	,,	green vitriol.
Hydrochloric acid (HCl)	,,	*spirit* of salt.
Ammonia (NH_3)	,,	*spirit* of hartshorn.

SUMMARY.

1. The numerical value attached to the "atomic weight." Compare with this the "equivalent," which may be defined as the weight of an element effecting the replacement of the unit weight of hydrogen.
2. The equivalent may be experimentally determined—
   (*a*) by measurement of the hydrogen evolved when a hydrogen salt (an acid) is acted on by a metal;
   (*b*) by replacement of a metal, in a solution of one of its salts, by another metal;
   (*c*) by reduction of an oxide in hydrogen, and determining the relation between the weight of the metal so obtained as compared with the weight of hydrogen employed to effect the reduction.
3. Where the element combines with oxygen in more than one proportion, forming oxides, say of the type M_2O, M_2O_2, etc., or of the type MO, M_2O_3, M_3O_4, etc., the equivalent obtained shows different values.

   The same applies in case the element forms more than one series of salts, *e. g.*

   MCl MNO_3 M_2SO_4 *ous* salts.
   MCl_2 $M(NO_3)_2$ MSO_4 *ic* salts.

   or—

   MCl_2 $M(NO_3)_2$ MSO_4 *ous* salts.
   M_2Cl_6 $M_2(NO_3)_6$ $M_2(SO_4)_3$ *ic* salts.

   The numerical relations between the atomic weight and the values for the equivalent are always of a simple nature.
4. The name applied to a compound of two elements usually indicates the elements which go to form the compound, and the relative number of their atoms entering into a molecule of the compound.
5. Where only two compounds exist having similar components they may be distinguished by the simple application of the ending *ous* and *ic*. And similarly these terminations suffice to distinguish the two series of salts which some elements form.
6. Basic oxides combined with water are termed *hydroxides.*

Acid oxides combined with water are termed *acids*.

Salts are formed by the union of hydroxides with acids.

The endings *ous* and *ic* as well as *ite* and *ate* are used in a special sense corresponding to what has been already stated in paragraph (5).

7. Though it is usual to adopt a systematic nomenclature in accordance with the principles laid down, many of the common names used before the adoption of any set rules still survive.

QUESTIONS.—CHAPTER X.

1. Define *atomic weight* and *equivalent.* Write down the atomic weight and equivalent of sodium, zinc, hydrogen, calcium, chlorine and nitrogen.
2. Give two independent methods of determining the equivalent of copper in copper sulphate.
3. How may the weight of hydrogen evolved by acting on sulphuric acid with metallic zinc be directly determined?
4. What weight of hydrogen should be evolved by dissolving 1·2 grammes of magnesium in excess of dilute sulphuric acid?
5. How is the equivalent of sodium determined?
6. Explain what takes place when a plate of metallic iron is dipped into a solution of copper sulphate.
7. A current of electricity is passed for the same time and under similar conditions through acidulated water and through a solution of sulphate of silver; if the weight of silver deposited be 0·54 gramme, what ought to be the weight of hydrogen and of oxygen evolved from the water?
8. What are the equivalents of iron in $FeCl_2$ and $FeCl_3$, and of copper in Cu_2O and CuO, and of sulphur in SO_2 and SO_3?
9. What is meant by a *binary* compound? State the terminations used in the denomination of binary compounds, and the significance of each.
10. Write down the formulæ of cuprous oxide, ferrous chloride, potassium sulphite, potassium sulphate, ferrous sulphide, nitrous acid, nitric acid, sulphuric anhydride.

CHAPTER XI.

SULPHUR AND SULPHUR DIOXIDE.

Occurrence of sulphur.—Sulphur is one of the comparatively few elements which occur in quantity in the uncombined condition. In Europe it is found in the neighbourhood of active or extinct volcanoes in Italy, Sicily, Iceland, etc., being usually associated with earthy matter. In combination with hydrogen it is found as sulphuretted hydrogen in certain mineral springs, and with metals as mineral sulphides, such as iron pyrites, FeS_2 ; galena, PbS ; zinc blende, ZnS; and cinnabar, HgS. Sulphates of lime (gypsum) and barium (heavy spar) also occur in some localities in considerable quantity. We see then that sulphur either free or in combination is widely distributed.

Extraction of sulphur.—Sulphur melts at 115° C., and in the molten condition can be run off from the earthy impurities and obtained in a state of moderate purity. It boils at 440° C., giving off brownish-red vapours which readily condense again on cooling, and the further purification of the sulphur may be effected by distillation in an iron retort, the vapours being passed into a brick chamber where they condense. (Fig. 22.) At the outset when the chamber is cool, the product obtained is a fine powder, called "flowers of sulphur," for just as water vapour at temperatures below zero (the melting-point of ice) condenses in the form of snow, so in the case of sulphur there is formed by rapid cooling, finely divided sulphur.

When the temperature of the chamber rises above the melting-point of sulphur (115° C.), the product of the condensation is *liquid* sulphur, and this is run off into moulds where it is cast into sticks known familiarly as "brimstone."

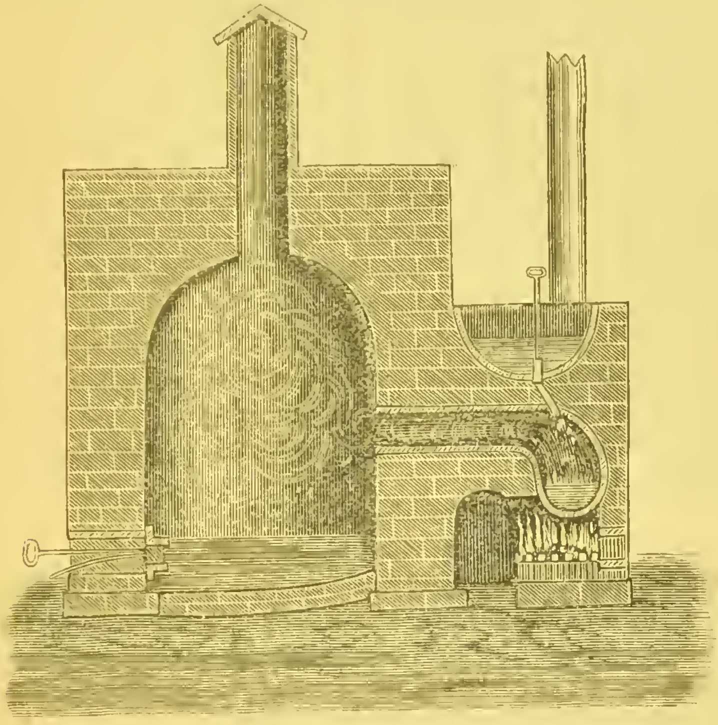

FIG. 22.

Sulphur is largely used in the arts in the production of matches, gunpowder, sulphuric acid, and as a source of sulphurous acid for bleaching wool, straw, and silk.

Physical changes of sulphur under the action of heat.

Exp. 62.—Put about 30 grammes of sulphur in a wide test-tube, and heat it as evenly as possible in the flame of a Bunsen burner. At 115° C. it will be seen to melt, and at a slightly higher temperature it forms a limpid liquid of a pale yellow colour. As it gets hotter the liquid grows more viscid and darker in colour, this stage occurring between 120° C. and 250° C. Above 250° C. it again becomes more mobile, and at 440° C. it boils and gives off a brownish-red vapour whose density is 96 times that of hydrogen (the molecule, S_6, see p. 62), and when this vapour is heated to 1000° C. its density is only 32 times that of hydrogen (the molecule, S_2, see p. 62). Pour some of the sulphur at about 350° C. in a thin stream into a beaker of water, and note the production of plastic sulphur.

Allotropic modifications of sulphur.—Some elements, notably sulphur, carbon, and phosphorus, show different properties, according to the particular treatment to which they have been subjected, and the conditions under which they have passed into the solid form. The differences observed are chiefly of a physical nature, relating to specific gravity, hardness, melting-point, solubility, and the like, but accompanying these there are variations in chemical behaviour towards reagents. The varieties of form which show such differences of physical character, or of chemical behaviour, are termed *allotropic* modifications.

Sulphur exists in the *crystalline* form, showing two allotropic modifications.

(1) Octahedral sulphur.
(2) Prismatic sulphur.

It exists also in the *plastic* form, a third allotropic modification obtained by suddenly cooling the molten sulphur, when at the temperature of about 350° C. it passes from the condition of a viscid liquid to the more mobile form. *Amorphous* sulphur, often called "milk of sulphur," is perfectly white and quite insoluble in bisulphide of carbon. This constitutes a fourth allotropic modification of sulphur.

Octahedral sulphur.—Sulphur is found naturally in rhombic pyramids rather like octahedra, and it is in this form that it separates out from solvents, such as bisulphide of carbon, on slow evaporation. The specific gravity of rhombic sulphur is 2·045.

Prismatic Sulphur.—Sulphur in this form is no longer rhombic, but monoclinic; it is also of lower specific gravity, 1·93, and melts at 120° instead of 115°, and when left at the ordinary temperature for some time, breaks up and passes into the more stable rhombic form, as, indeed, all the modifications tend to do.

Exp. 63.—Melt about 500 grammes of sulphur in a clay crucible, and allow it to cool until a crust forms at the surface; the crust is then pierced and the still liquid portion poured out. Beneath the crust will be found long prismatic needles of sulphur.

Plastic sulphur.—In the crystalline form, sulphur is brittle, but in the plastic condition, as the name implies, it can be moulded with the fingers, or drawn out into long flexible threads. Unlike the modifications previously described, it is only partially soluble in bisulphide of carbon. On standing, it slowly hardens and passes into the ordinary form of sulphur.

Amorphous sulphur.—This modification is devoid of any definite structure, and consists of an impalpable powder, the particles of which are often so small that they pass through filter paper. It has a lower specific gravity (1·82) than prismatic sulphur, and is insoluble in bisulphide of carbon.

Exp. 64.—Make a moderately concentrated solution of sodium thiosulphate, or of an alkaline sulphide (*e.g.* solution of ammonium sulphide), and add a few drops of hydrochloric acid. The solution becomes turbid, and a white precipitate of "milk of sulphur" is produced.

$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + S + SO_2 + H_2O.$$

Sulphur combines with many elements when heated with them. Thus it burns in oxygen at about 400° C., and it combines with carbon at a red heat, forming carbon disulphide CS_2: while chlorine and hydrogen passed into boiling sulphur give sulphur monochloride S_2Cl_2, and sulphuretted hydrogen respectively.

Many metals combine with sulphur when heated with it; for example iron (see Exp. 6), silver, forming silver sulphide Ag_2S, and copper, forming cuprous sulphide Cu_2S.

Exp. 65. Heat sulphur to the boiling-point and until the upper part of the tube is filled with its vapour, and then plunge thin sheet copper, or Dutch metal, into the vapour; the metal glows, and enters into combination with the sulphur to form sulphide of copper.

SULPHUR DIOXIDE, SO_2.—When sulphur burns in air or oxygen, sulphur dioxide is formed, and for purposes in which admixture with nitrogen or the excess of oxygen is of no moment, the gas may be prepared by this method. On the manufacturing scale indeed sulphur dioxide is sometimes so obtained, though more usually a sulphide containing a large proportion of sulphur such as iron pyrites, FeS_2, is employed (see p. 127).

Preparation of sulphur dioxide.—When the gas is required in a tolerably pure condition the following method is applicable—

> **Exp. 66.**—About 20 grammes of metallic copper are placed in an eight-ounce flask provided with a thistle funnel and delivery tube, and 50 c.c. of concentrated sulphuric acid are poured down the funnel. The flask is then heated on a sandbath, moderating the heat so soon as the action commences. The reaction which takes place is a complex one, but consists essentially in the reduction of the sulphuric acid by copper.

Mercury, charcoal, or sulphur may be substituted for copper, but in the case of charcoal the gas which passes off is mixed with carbon dioxide—

$$C + 2\ H_2SO_4 = CO_2 + 2\ H_2O + 2\ SO_2.$$

With sulphur the reaction is—

$$S + 2\ H_2SO_4 = 2\ H_2O + 3\ SO_2,$$

sulphur dioxide being formed both from the sulphur itself and from the sulphuric acid used. It remains to be added that all sulphites when treated with a mineral acid yield sulphur dioxide—

$$\underset{\text{Sodium sulphite.}}{Na_2SO_3} + 2\ H_2SO_4 = \underset{\text{Sodium hydrogen sulphate.}}{2\ NaHSO_4} + H_2O + SO_2.$$

Sulphur dioxide being very soluble in water cannot be collected over this liquid, mercury may however be used, but as it is more than twice as heavy as air it may be conveniently collected by displacement of air. Several jars may be filled with it, and its properties demonstrated by the experiments given below.

Properties.—Sulphur dioxide is a heavy colourless gas having a suffocating odour. At 760 m.m. pressure, water at zero dissolves 80 times its volume of the gas, and at 10° C. 56 times its volume, the solution having an acid reaction. Sulphur dioxide condenses to a liquid under ordinary atmospheric pressure at − 8° C., and under 2 atmospheres pressure at 0° C. It can therefore be obtained in the liquid form by passing the gas into a vessel surrounded by a freezing mixture of ice and salt.

Exp. 67.—Put a lighted taper into a jar of the gas, it will be extinguished, nor will the gas itself burn. Metallic potassium when previously ignited will however burn at the expense of the oxygen in this gas.

Exp. 68.—Show the great solubility of the gas by the method used in experiment 32 (page 42), or by passing the gas through 10 c.c. of water until a saturated solution is obtained. Note the acid properties of the solution, and that it possesses the odour of the gas.

As *oxidizing agents* are those which readily transfer oxygen to other substances which are thereby subjected to oxidation, so *reducing agents* are those which take away oxygen and effect reduction. Sulphur dioxide is a typical reducing agent; its powers as an antiseptic and as a medium for bleaching silk, straw and wool being due to its affinity for oxygen. Chlorine bleaches in consequence of its bringing about the oxidation of the colouring matter; sulphur dioxide bleaches, on the contrary, in consequence of its reducing action. The one liberates *oxygen* from water—

$$Cl_2 + H_2O = 2\,HCl + \underset{\text{Nascent oxygen.}}{O}$$

the other liberates *hydrogen*—

$$\underset{\text{Sulphurous acid.}}{H_2SO_3} + H_2O = \underset{\text{Sulphuric acid.}}{H_2SO_4} + H_2$$

Exp. 69.—Rose-leaves thrown into a solution of sulphur dioxide are bleached, the colouring matter however is not destroyed as when chlorine is used, and the colour may even be restored again by adding a few drops of strong sulphuric acid, or by exposure to air for some time.

Exp. 70.—Liberate iodine from potassium iodide by adding a *few drops* of chlorine water; now add sulphurous acid, and the brown colour of the iodine will disappear.

$$2\,KI + Cl_2 = 2\,KCl + I_2.$$
$$I_2 + H_2O + H_2SO_3 = H_2SO_4 + 2\,HI.$$

The sulphurous acid reduces water, and is itself oxidized to sulphuric acid, whilst the hydrogen which is liberated combines with the iodine to form hydriodic acid, which is colourless. A similar reaction takes place with chlorine water.

Exp. 71.—To a solution of potassium chromate add sulphurous acid, the *yellow* colour of the chromate will change to *green* owing to the reduction of CrO_3 to Cr_2O_3, the salts of the former being red or yellow, whilst those of the latter are green. This change from yellow to green affords a means of testing for the presence of sulphur dioxide either in the gaseous state or in solution.

Sulphurous acid and sulphites.—We have seen that sulphur dioxide dissolves readily in water, forming an acid, H_2SO_3. We may regard this as a salt of hydrogen (see page 109), or as formed by the union of water with sulphurous anhydride, SO_2. In acids which have been previously treated, such as HF, HCl, we have only had one atom of hydrogen which is replaceable by metals, and these are termed *monobasic* acids. In sulphurous acid we have two atoms of hydrogen so replaceable, affording an example of a *dibasic* acid; in phosphoric acid, H_3PO_4, we have a *tribasic* acid.

Sulphurous acid being dibasic forms two series of salts called sulphites, one in which *both* the hydrogen atoms are replaced, such as Na_2SO_3, K_2SO_3, $CaSO_3$, and these are termed *normal* sulphites, or sometimes *neutral* sulphites. The second series of salts are those in which only *one* hydrogen atom is replaced by a metal, such as $NaHSO_3$, $KHSO_3$, $CaH_2(SO_3)_2$, the *acid* sulphites; $NaHSO_3$ is, for instance, called acid sulphite of soda, or bisulphite of soda, or regarding sulphurous acid as a hydrogen salt, it may be termed sodium hydrogen sulphite. They may be prepared by passing SO_2 into solutions containing the basic hydroxide or carbonate.

Exp. 72.—Take 50 c.c. of a solution of caustic soda, and pass sulphur dioxide into it till it is saturated with the gas. On allowing the solution to evaporate at ordinary temperatures (it decomposes when heated), or on adding alcohol to it, the *acid salt*, sodium hydrogen sulphite, separates out—

$$NaOH + SO_2 = NaHSO_3.$$

If we add a second 50 c.c. of the same solution of caustic soda we shall then obtain on evaporation or treatment with alcohol the *normal* salt—

$$NaOH + NaHSO_3 = Na_2SO_3 + H_2O.$$

In a similar way, substituting caustic potash instead of soda, the sulphites of potash may be prepared. The normal sulphites of all other metals excepting the alkalies are insoluble in water, and may be obtained as precipitates by the addition of a soluble salt of the metal to a solution of an alkaline sulphite.

$$CaCl_2 + Na_2SO_3 = CaSO_3 + 2\,NaCl.$$

Sulphites slowly take up oxygen from the air, passing into sulphates, and all sulphites are decomposed by acids with evolution of SO_2.

SUMMARY.

(1) Natural occurrence of free sulphur in volcanic regions and in combination as mineral sulphides and sulphates. Separation of sulphur from associated mineral matter by distillation.

(2) *Allotropic forms* of solid sulphur—

	Form.	Solubility.	Sp. gr.	Melting point.
Amorphous	Fine powder, Milk of sulphur	Insoluble in CS_2.	1·82	115°C.
Crystalline (1)	Rhombic pyramids	Soluble in CS_2.	2·05	115°C.
(2)	Monoclinic prisms	„ „	1·93	120°C.
Plastic	Amorphous	Partly soluble in CS_2.	—	—

(3) Sulphur melts at 115° C. and passes through several variations of colour and viscosity as the temperature rises, finally boiling at about 440° C. The vapour at 500° C. is 96 times the density of hydrogen and at 1000° C. its density is $\frac{1}{3}$ of this.

(4) *Sulphur dioxide.*

Preparation.—

- (*a*) from sulphur or iron pyrites (FeS_2).
- (*b*) by action of Cu, Hg, C, or S on H_2SO_4.
- (*c*) by action of a mineral acid on a sulphite.

(5) *Properties.*—

- (*a*) Great solubility—forming sulphurous acid.
- (*b*) Over twice as heavy as air—odour.
- (*c*) Readily condensed to liquid.
- (*d*) Non-combustible and non-supporter of combustion.
- (*e*) Reducing agent owing to facility with which it takes up oxygen.
- (*f*) Bleaches certain vegetable colours.
- (*g*) Formation of soluble and insoluble sulphites.

QUESTIONS.—CHAPTER XI.

1. How is sulphur separated from the mineral matter with which it is associated in the native condition?
2. Under what conditions are "flowers" of sulphur and "milk" of sulphur formed?
3. Describe the physical changes through which sulphur passes when it is heated in the absence of air.
4. Explain what you understand by "allotropic modification."
5. Tabulate the properties of the different allotropic modifications of sulphur so as to bring out the differences between them.
6. What is the action of hydrochloric acid on sodium thiosulphate on calcium sulphide, and on ferrous sulphide?
7. What is the action of sulphur vapour on heated copper, iron, oxygen, and hydrogen respectively? Give equations representing the changes which occur.
8. Describe how sulphur dioxide is prepared on the laboratory scale and how it is collected.
9. State the *physical* properties of sulphur dioxide. What volume of the gas will dissolve in 100 c.c. of water at 10° C. under normal pressure?
10. Explain the bleaching action of sulphur dioxide, and show in what respects it differs from that of chlorine.
11. A little chlorine is passed into a solution of potassium iodide, and then afterwards sulphur dioxide is passed in; state the changes which take place and give equations representing them.
12. Describe the preparation of the normal and acid sulphites of soda; what is the action of sulphuric acid on them?

CHAPTER XII.

SULPHUR TRIOXIDE, AND SULPHURIC ACID.

Sulphur trioxide, SO_3.—This body occurs in small quantity with the sulphur dioxide formed during the combustion of sulphur or iron pyrites.

Preparation.—Sulphur dioxide and oxygen are passed over platinum sponge, obtained by igniting the double chloride of ammonium and platinum. The gases must be dry, and the platinum sponge gently heated, and there then appear at the exit, dense white fumes, which if passed into a cool dry receiver condense to white silky needles of sulphur trioxide.

A second method which is employed in the production of sulphur trioxide in large quantities is based on the decomposition of ferrous sulphate, $FeSO_4. 7 H_2O$. This body, when heated, first loses most of its water of crystallization. The partially dehydrated salt more strongly heated is decomposed thus—

$$2 FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

The water which still remains attached to the salt, however, combines with some of the SO_3 forming sulphuric acid, H_2SO_4, and this takes up another molecule of SO_3 forming $H_2S_2O_7$—

$$H_2O + SO_3 = H_2SO_4 \text{ and } H_2SO_4 + SO_3 = H_2S_2O_7.$$

The acid thus produced is known as Nordhausen sulphuric acid; it differs from ordinary sulphuric acid, in that it fumes when exposed to moist air, and is often termed *fuming sulphuric acid.* This liquid which condenses from the distillation of partially dehydrated ferrous sulphate, when removed from the receiver and heated, yields the SO_3 which it has taken up, leaving behind sulphuric acid.

By distilling with a powerful dehydrating agent, such as phosphorus pentoxide, the elements of water may even be removed from sulphuric acid itself, and this affords a third method whereby SO_3 may be obtained—

$$P_2O_5 + H_2SO_4 = 2\ HPO_3 + SO_3.$$

Properties of sulphur trioxide.—At ordinary temperatures sulphur trioxide forms white transparent needles, which melt at 15° C., and boil at 46° C.; at a red heat it breaks up into sulphur dioxide and oxygen. It combines very eagerly with water, evolving much heat, and in contact with water it gives a hissing sound like that of the quenching of hot iron. Sulphuric acid is thereby formed; it is of interest to add that it enters into direct combination with certain oxides, forming sulphates, *e.g.* with baryta, BaO, it yields barium sulphate, $BaSO_4$.

SULPHURIC ACID, OR OIL OF VITRIOL, H_2SO_4. We have seen that under certain circumstances sulphur dioxide combines with oxygen to form sulphur trioxide, and that this in presence of water gives sulphuric acid. The oxidation of sulphurous acid to sulphuric acid also takes place slowly when its aqueous solution is exposed to air at ordinary temperatures.

Such methods are, however, not suitable for the production of large quantities[1] of sulphuric acid as an article of commerce.

The oxidation of sulphurous acid is effectually performed by the intervention of the oxides of nitrogen, and on the large scale sulphur dioxide, oxygen (supplied in the form of air) and steam are brought together, and these in presence of oxides of nitrogen form sulphuric acid.

The *sulphur dioxide* in works where a very pure acid is made is obtained by burning brimstone, but in the very large majority of cases iron pyrites is used as the source of the gas. This is burnt in a series of "kilns," and the heat arising from the combustion is sufficient to render the operation continuous, fresh charges being added from time to time.

$$2\ Fe\,S_2 + 11\ O = Fe_2O_3 + 4\ SO_2.$$

---

[1] Over a million tons of oil of vitriol are produced in Great Britain alone in the course of a year.

The *nitric acid* from which the oxides of nitrogen are derived is prepared by the action of concentrated sulphuric acid on Chili saltpetre, $NaNO_3$—

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3;$$

the acid fumes are carried into the flues along which the sulphur dioxide and air pass, and there intermingle with these gases.

The *air* is drawn in through the pyrites burners or kilns, the draught being maintained by means of a chimney, and by adjustment of the doors of the kilns so as to admit the quantity of air which experience has shown to be necessary.

The *steam* is supplied from low pressure boilers, and introduced into the "chambers" in such a way as to become intimately associated with the other products.

The reaction ending in the production of sulphuric acid does not take place under the circumstances very rapidly, and it is necessary to provide for a lengthened period of contact between the various bodies which take part in it. The gases are led into a series of large chambers where they meet with the steam. These are usually two or three in number, and have a total capacity of 100,000 to 150,000 cubic feet, the relation of the sulphur burnt to the capacity of the chamber being such that the average time occupied by the gas in traversing the chambers is something like three hours. The walls and floor of the chambers are constructed of sheet-lead supported on a wooden framework, lead being a metal which is scarcely attacked at all by sulphuric acid of the strength produced in the chambers. The chambers are kept cool enough to serve as condensers, so that the acid collects on the floor, and is drawn off periodically.

The recovery of the oxides of nitrogen.—In practice, the higher oxides of nitrogen are carried forward in the chambers, and would escape at the exit. To avoid this waste, advantage is taken of the fact that they are absorbed by *concentrated* sulphuric acid. The exit gases from the chambers are therefore passed through a tower (known as the *Gay-Lussac tower*), packed with coke, down which concentrated sulphuric acid constantly trickles. The oxides of nitrogen taken up in this way are discharged again if the acid be diluted, since they are practically insoluble in *dilute* sulphuric acid.

In order therefore to render these absorbed gases again available in the production of sulphuric acid, the acid which has traversed the Gay-Lussac tower is pumped up to the top of a *Glover tower* placed at the entrance of the chambers. This tower is packed with flints and coke, and the nitrated acid is diluted as it runs down by being mixed with the weaker "chamber acid." The oxides of nitrogen which have been absorbed in the Gay-Lussac tower are thus discharged within the Glover tower, and there mix with the gases which are passing from the pyrites burners to the chambers, the Glover tower being placed between the pyrites burners and the chambers. The Glover tower performs the further function of cooling the gases before they enter the chambers, and in addition to this, a considerable amount of sulphuric acid is actually formed in the Glover tower itself. The acid which escapes from the Glover is strong (80 per cent.), and has a temperature of 120° to 130°.

Details relating to Sulphuric Acid plant. Fig. 23.

(1) **Pyrites burners.**—These are shown partly in section, so as to indicate the charge and the common flue into which the gas passes. There are 24 burners, a second row of 12 being placed back to back with those shown. The various doors on the front of the burners serve for charging the ore, stirring the charge when necessary, and finally for removing the burnt ore which has fallen into the ashpit underneath.

(2) **The Glover tower.**—This is packed with flints and coke, through which trickle from the tanks above (*a*) strong nitrated acid, which has been previously used to absorb nitrous fumes in the Gay-Lussac tower, (*b*) weak chamber acid. When the two acids mix, nitrous fumes are freely liberated within the tower, and thus it supplements the nitre-pots in providing the nitrous fumes necessary for the process.

(3) **The Gay-Lussac tower.**—This is packed with coke, and the strong acid (sp. gr. 1·78) which is supplied from the tank above, passes over the coke and absorbs any nitrous fumes in the exit gases from the chambers.

The course taken by the gases.—The sulphur dioxide and

PLANT FOR MANUFACTURE OF SULPHURIC ACID. SCALE 8 FT. TO THE INCH.

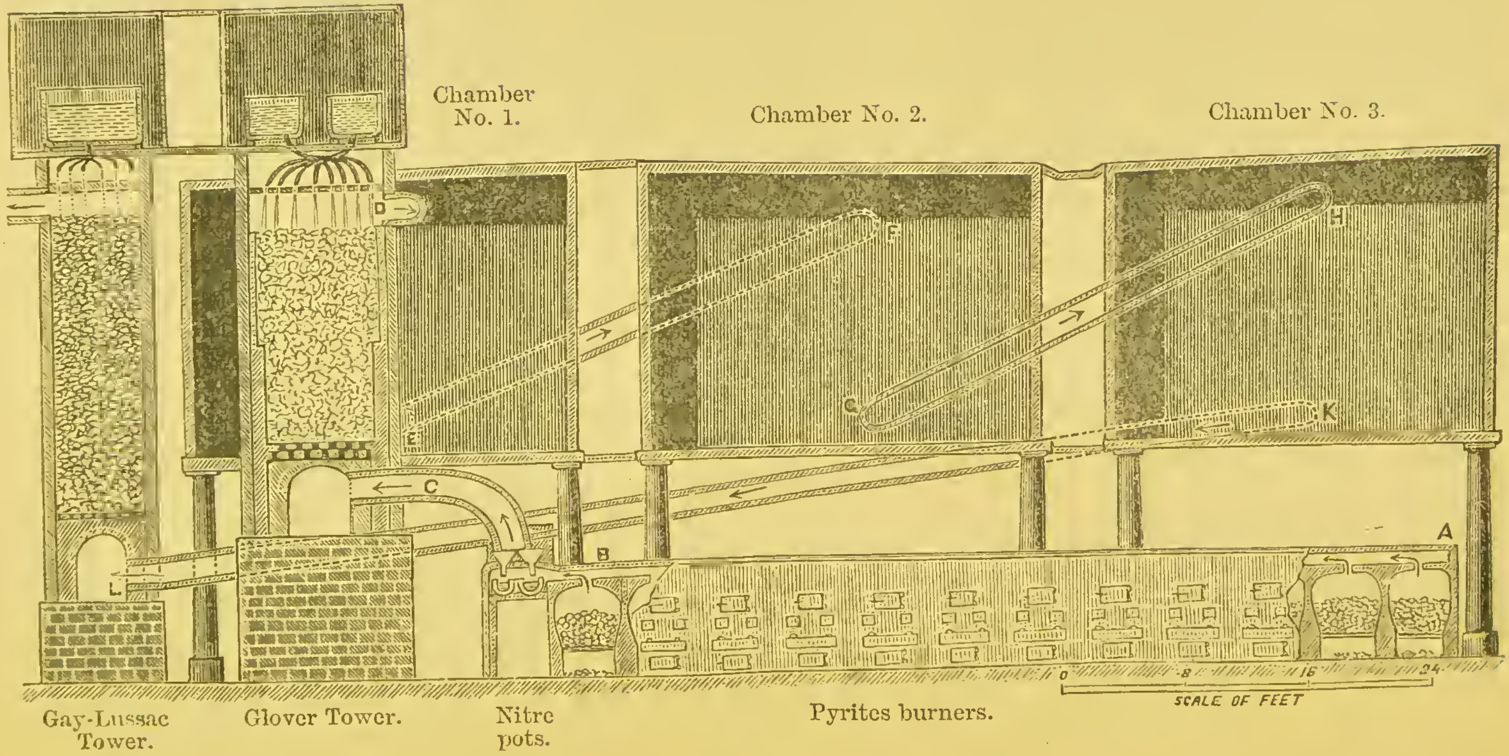

FIG. 23.

air (in excess) pass along the common flue A B from the pyrites burners over the nitre-pots, and then along the pipe C, through the Glover tower. At D they pass in at the front of chamber No. 1, and thence from the back at E to the back of chamber No. 2, entering this at F by the pipe E F. Similarly by G H from the front of chamber No. 2 to the front of No. 3, and from the back of this to the base of the Gay-Lussac tower by K L. Having traversed the Gay-Lussac tower the exit gas finally passes off to the chimney by the outlet at the upper part of the tower. The steam is blown in at the ends of the chambers in such a way as to travel always in the direction of the draught, that is to follow the same course as that taken by the gases. Each chamber is 25 ft. wide, 20 ft. high, and 100 ft. long, and they are seen in the figure in transverse section, so that the direction of the length would be perpendicular to the plane of the paper.

The functions of the various parts of the sulphuric acid plant may be summed up thus—

The Chambers (1) bring about a prolonged contact between the reacting bodies.

(2) Condense the sulphuric acid which collects as the chamber acid (sp. gr. 1·6, containing nearly 70 per cent. H_2SO_4) on the floor of the chamber.

The Gay-Lussac Tower absorbs the oxides of nitrogen in the *exit* gases from the chamber.

The Glover Tower (1) effects discharge of oxides of nitrogen from the nitrated acid produced in Gay-Lussac tower.

(2) Cools the gases from the pyrites burners, the heat so absorbed concentrating the acid to sp. gr. 1·75, or 80 per cent.

(3) Assists in the actual production of sulphuric acid.

At a higher degree of concentration sulphuric acid rapidly attacks lead, and if stronger acid is needed, the concentration is effected by boiling it in glass or platinum stills, when *very weak* acid passes over, and the acid remaining in the still rises in strength till it contains 95 to 98 per cent. H_2SO_4.

Acid containing 100 per cent. H_2SO_4 cannot be obtained by distillation alone. It is prepared by adding sulphur trioxide to the 98 per cent. acid, and then on freezing, crystals of pure H_2SO_4, melting at 10° C., separate out.

Properties of sulphuric acid.—The pure concentrated acid is a thick oily liquid (sp. gr. 1·84), from whence it derives the name, *oil* of vitriol. It boils at 338° C., with partial decomposition, so that when the acid containing 100 per cent. H_2SO_4 is distilled the residue becomes weaker, until it reaches a strength of about 96 per cent. H_2SO_4, at which it remains constant.

It is highly corrosive, charring wood and many organic substances even at the ordinary temperature. This is largely owing to the great avidity with which it takes up water. Wood consists mainly of cellulose, a compound of carbon, and hydrogen and oxygen in the proportions in which they are contained in water: the acid therefore abstracts water, leaving a mass of carbon. The concentrated acid is frequently used for drying the ordinary gases. Its affinity for water is likewise shown by the large amount of heat evolved when the two liquids are mixed.

Laboratory representation of the Sulphuric Acid Manufacture.

The formation of sulphuric acid may be represented in the laboratory by taking a large flask (5 litres) and fitting it with a cork provided with five holes through which pass tubes delivering—

(1) Sulphur dioxide (for preparation see p. 120),
(2) Nitric oxide („ „ „ p. 153),
(3) Steam,
(4) Oxygen from a gasholder;

while the fifth hole is provided with a tube opening into the air. The arrangement is shown in the figure.

Pass some sulphur dioxide, nitric oxide, steam, and oxygen into the flask, then shut off the steam supply; crystals of nitrosulphonic acid (lead chamber crystals) may be seen to form. On clearing the flask of red fumes by a current of oxygen, and then passing in more steam, these crystals will dissolve with the evolution of red fumes. After allowing the reaction to go on for some minutes, the liquid condensed in the flask may be tested for sulphuric acid (see p. 133).

The sulphates.—Concentrated sulphuric acid in presence of metals frequently undergoes partial reduction, sulphur dioxide being evolved (see p. 120), but with basic oxides it reacts with great energy and forms a series of salts called the sulphates.

The sulphates of lead, calcium, barium, and strontium are insoluble or only slightly soluble in water, the rest being readily soluble. Sulphuric acid like sulphurous acid forms two classes of sulphates, the *normal* sulphates such as Na_2SO_4, $CaSO_4$, and the *acid* sulphates such as $NaHSO_4$, either one or the other being formed according to whether the base or the acid are in excess.

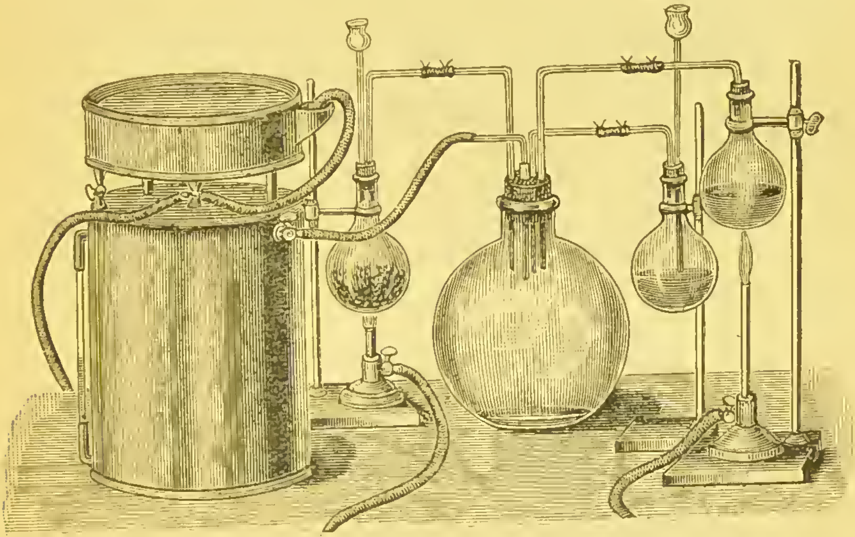

FIG. 24.

Test for Sulphates.

Exp. 73.—Add barium nitrate to a solution which contains either sulphuric acid or a sulphate in presence of hydrochloric acid: a white precipitate is formed consisting of sulphate of barium. This is the only common barium salt which is insoluble in water and acids, and the formation of the precipitate is therefore characteristic, and may be taken as a sure indication of the presence of sulphuric acid either in the free state or in combination.

SUMMARY.

Sulphur trioxide.

(1) *Preparation.*—

(*a*) by direct union of SO_2 and oxygen
- (1) in presence of spongy platinum.
- (2) in presence of oxides of nitrogen.

(*b*) by action of heat on certain sulphates.

(*c*) „ „ phosphorous pentoxide on sulphuric acid.

(2) *Properties.*—

(*a*) White needle-like crystals.

(*b*) Great affinity for water—forming H_2SO_4.

(*c*) „ „ „ certain oxides—forming sulphates.

Sulphuric acid.

(1) *Preparation.*—

By interaction of oxygen (air) SO_2 and steam in presence of oxides (or oxyacids) of nitrogen.

(2) *Properties.*—

(*a*) Heavy oily liquid, sp. gr. 1·84.

(*b*) Boils at 338° C., with partial decomposition.

(*c*) Crystals having the composition H_2SO_4 separate at low temperatures; these melt at 10° C.

(*d*) Highly corrosive, chiefly owing to its great affinity for water,—chars organic substances.

(*e*) Powerful desiccating agent.

(*f*) Formation of soluble and insoluble sulphates.

QUESTIONS.—CHAPTER XII.

1. Under what circumstances does sulphur dioxide combine with oxygen?
2. What is the action of heat on $FeSO_4, 7 H_2O$?
3. How may sulphur trioxide be obtained from (*a*) Nordhausen sulphuric acid; (*b*) ordinary sulphuric acid?
4. Describe how sulphur dioxide becomes transformed into sulphuric acid on the large scale.
5. Describe the general construction and the functions of the lead chambers used in the manufacture of sulphuric acid.
6. How is sulphur dioxide obtained for the manufacture of sulphuric acid, and what means are employed to ensure its being mixed with the proper quantity of air?
7. What is the part played by the Glover tower in the production of sulphuric acid?
8. How are the oxides of nitrogen, which are found in excess towards the exit of the chambers, recovered?
9. What is "chamber" acid, and how is concentrated acid obtained from this?
10. Write down the formulæ of the normal sulphates of copper, potassium, lead, iron, and aluminium.
11. Give a method of testing for the presence of a soluble sulphate, and show how you would distinguish whether an aqueous solution contained—
    (*a*) free sulphuric acid only,
    (*b*) a neutral sulphate,
    (*c*) a mixture of the two.

CHAPTER XIII.

NITROGEN—THE ATMOSPHERE—AMMONIA.

NITROGEN is the first member of a group of elements, nitrogen, phosphorus, arsenic, antimony, and bismuth, which either in themselves or their compounds exhibit considerable analogy to one another. The first two members only are usually classed with the non-metals.

The elements forming this group show a transition in physical properties as the atomic weight increases, nitrogen being gaseous at the ordinary temperature, whilst phosphorus is solid but easily vapourized, the other members being more difficult to volatilize.

Speaking more particularly with regard to nitrogen and phosphorus, it will be seen by a comparison of their chief compounds that they resemble one another—

(1) in forming hydrides of similar composition NH_3, PH_3, both of which combine directly with haloid acids.

(2) in forming a characteristic series of oxides some of which yield powerful acids.

Occurrence.—Nitrogen occurs mixed with oxygen in the atmosphere, of which it forms nearly four-fifths the volume.

Although it does not enter to any large extent into the composition of animal and vegetable tissues, it is, notwithstanding, a very constant and essential constituent of such tissues. The nitrogen of plants is obtained chiefly through the medium of the soil, in which nitrates and ammonium salts always occur. Animals cannot assimilate nitrogen directly, and derive their supply from the plants.

Recently, the investigations of Ramsay and Rayleigh have established the existence of a new gas in the atmosphere. This gas has been named argon, and it remains associated with the nitrogen after the oxygen has been removed, constituting nearly 1 per cent. of the air; it is exceedingly inert, and is only separated from the nitrogen with great difficulty.

Preparation.—Air may be deprived of oxygen either by burning phosphorus in it or by passing it over red-hot copper, the oxygen combining to form phosphorus pentoxide and cupric oxide respectively.

Exp. 74.—Float a small porcelain crucible containing red phosphorus on water, and place a large bell-jar with a narrow neck (Fig. 25) over it, and so that the depth of the water is about one-third the

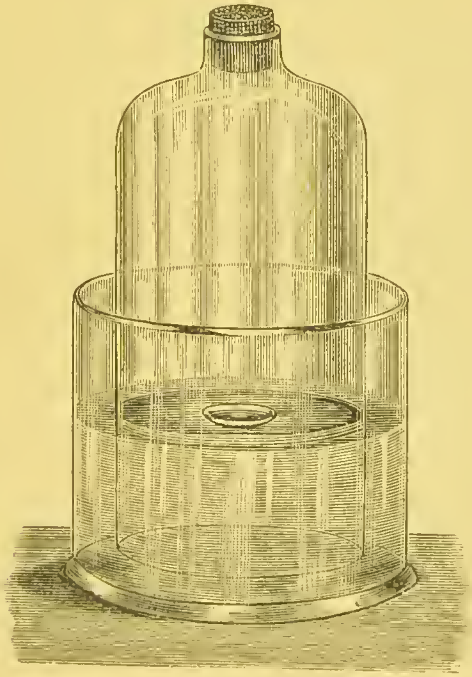

Fig. 25.

height of the bell-jar. Now ignite the phosphorus by touching it with a hot wire, and close the bell-jar by means of a cork or stopper. The phosphorus will burn brightly at first, and the heat evolved will expand the gas and depress the water inside the jar. After a little time the combustion will cease, and the water ultimately rise further than its original level. The fine white powder which is formed during the combustion, consisting of phosphorus pentoxide, will gradually settle down and dissolve in the water. When the water has ceased to rise within the jar, pour more water into the vessel in which it stands until the levels inside and outside are the same. The gas has diminished in volume and altered in character. It will be found to extinguish a lighted taper, and to be quite inert towards chemical reagents. When air is deprived of its oxygen, the residual gas which we have now in the jar is nitrogen.

A second method of preparation consists in heating ammonium nitrite, which breaks up into water vapour and nitrogen.

$$NH_4NO_2 = N_2 + 2\ H_2O.$$

A third method is to act on concentrated solution of ammonia (taking care to keep a large excess of ammonia present throughout the experiment) with chlorine—

$$8\ NH_3 + 3\ Cl_2 = N_2 + 6\ NH_4Cl.$$

This reaction may be represented in two stages—

$$2\ NH_3 + 3\ Cl_2 = N_2 + 6\ HCl$$
$$6\ NH_3 + 6\ HCl = 6\ NH_4Cl.$$

If the ammonia be not kept in excess the reaction is

$$NH_3 + 3\ Cl_2 = NCl_3 + 3\ HCl,$$

the nitrogen trichloride being a heavy liquid which is liable to explode in a very dangerous manner.

Properties of nitrogen.—Nitrogen is a colourless, tasteless gas, which is unable to support life or combustion. Nitrogen does not combine with oxygen under ordinary conditions; but it may be made to do so by means of an alternating current of electricity, when the higher oxides of nitrogen are formed. It is somewhat lighter than air, and condenses to the liquid form at −193° C.; it is slightly soluble in water, less so than oxygen (see p. 83). It combines directly only with some few metals, such as magnesium, titanium, and iron, and on the whole is characterized by its great inertness.

THE ATMOSPHERE.—The gaseous envelope which surrounds the earth is chiefly composed of nitrogen and oxygen. With these are associated water vapour, carbon dioxide, ammonia, and other gases, the amounts of which vary according to circumstances. From whatever locality the air has been obtained, the relative proportions of nitrogen and oxygen show only slight variations, as the following results show.

Percentage of Oxygen by Volume.

72	analyses in different parts of Europe	(mean)	20·95
17	„ „ the Polar Seas	„	20·90
3	„ at elevation of 15,000 ft. or over	„	20·94

The determination of the composition of the atmosphere.—If a known volume of air, from which the impurities have been removed, be introduced into a eudiometer and exploded with about twice its volume of hydrogen (see p. 70), two volumes of hydrogen combine with one volume of oxygen to form water vapour, which condenses, and thus *one-third* the diminution in volume represents the volume of oxygen present.

The difference between this and the original volume of air taken is the volume of nitrogen.

An approximate determination of the composition by volume may be made in the following way.

Exp. 75.—Take a glass tube about 700 m.m. high and 15 m.m. diameter closed at one end, and of as even bore as possible. Invert this, filled with air, over water, note the volume of the air, and pass up into it a piece of phosphorus attached to a stout copper wire. The phosphorus will slowly combine with the oxygen of the air, and the water will rise in the tube. Allow it to stand in a shaded place until the water ceases to rise. Now remove the phosphorus, and adjust the level of the water to the same height inside and outside the tube, and note the volume of residual nitrogen. The volume (correction may have to be made for variation of temperature and pressure during the experiment) occupied by the original air and the residual nitrogen may be ascertained with tolerable accuracy by seeing what volume of water is required to fill the tube to the two levels noted.

The composition of air by *weight* may be ascertained by passing the air over red-hot copper, with which the oxygen

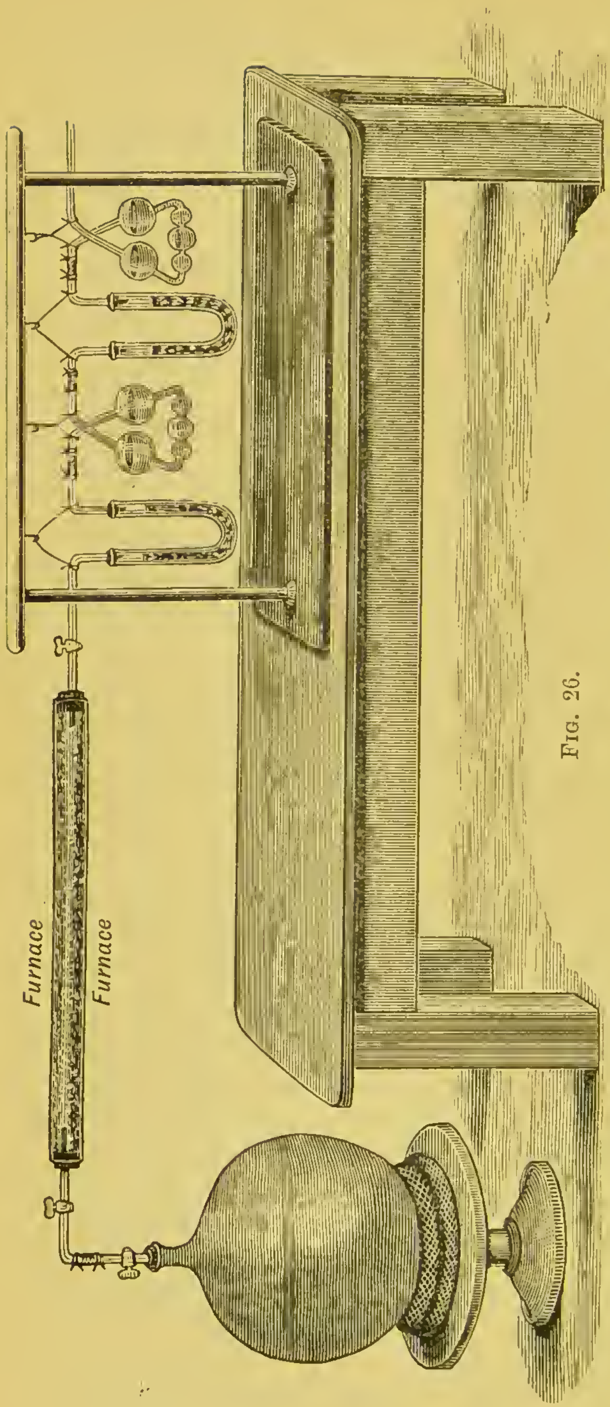

Fig. 26.

combines to form copper oxide. The air is previously freed from carbon dioxide and moisture, by being passed over potash and concentrated sulphuric acid. The apparatus used is shown in Fig. 26; it consists essentially of a large glass globe, to which is attached a tube containing metallic copper, and heated in a furnace. The globe is first rendered vacuous by means of a good air-pump, the stop-cock is closed, and the globe carefully weighed. The tube containing the copper is then rendered vacuous, closed and weighed. The copper having been heated to redness, the stop-cock is opened sufficiently to allow a slow current of purified air to pass through the tube and into the glass globe. On the way, it is deprived of its oxygen, and if the experiment has been carefully conducted, only nitrogen passes into the globe. After the apparatus has quite cooled, the globe is again weighed, and the increment gives *the weight of the nitrogen.* The tube is also weighed again, and the increase there shows *the* *weight of the oxygen*, together with a little nitrogen which remains in the tube. On exhausting and weighing again, the decrease in weight is added to the increase in weight of the globe to obtain the total nitrogen. The oxygen is given by the difference of the two weighings of the *exhausted* tube.

A series of such determinations gave the composition by weight of air as—

Nitrogen	76·995
Oxygen	23·005

Water vapour in air.—The amount of water vapour varies with the temperature and the degree of saturation of the air, for the higher the temperature of the air, the more moisture will it take up before it is saturated. The average amount is somewhat under 1 per cent. by volume, but in warm, moist climates may approach 4 per cent. It may be measured by observations on the dew-point (see text-books on physics), or by passing a known volume of air over calcium chloride contained in U tubes, and noting the increase in weight of the tubes.

The amount of water vapour which the air can contain may be judged by the fact that 1 cubic mile of air saturated at 35° would deposit, if cooled to 0°, 140,000 tons of rain. But while the air is seldom completely saturated, it never contains less than $\frac{1}{10}$ of the possible amount.

Carbon dioxide in air.—The amount of this gas in air varies considerably, according to the locality from which the sample of air is taken. In country air there are from three to four volumes of CO_2 in 10,000, but in towns the amount is larger, and may reach seven or eight volumes. In badly-ventilated dwellings even ten-fold the normal amount of carbon dioxide may occur. The determination of carbon dioxide is a matter of importance, especially in the case of indoor air, since it serves to show the efficiency of ventilation.

The presence of carbon dioxide in air may be shown by exposing lime-water in a shallow dish; the lime-water is soon covered with a thin pellicle, owing to the formation of calcium carbonate or chalk, which is insoluble in water—

$$CaO + CO_2 = CaCO_3.$$

Baryta water may, by Pettenkofer's method, be used as a means of determining the amount of carbon dioxide in air. A solution of baryta (which is alkaline) of known strength is shaken up with a measured quantity of air, say 10 litres; part of the baryta is converted into barium carbonate (a neutral body), whilst part remains unaltered. The amount of alkali (the baryta) is now smaller by reason of the conversion of part of it into carbonate by the carbon dioxide. The more carbon dioxide is present, the greater will be the amount of baryta converted into barium carbonate, and the greater will be the difference between the amount of alkali originally taken and that remaining afterwards. By ascertaining the amount of oxalic acid required to neutralize the original baryta water, and that required to neutralize the residual liquid, the quantity of carbon dioxide in the 10 litres of air may be ascertained.

Other impurities in air.—The remaining impurities, such as suspended dust and carbon, ammonia, sulphur compounds, hydrochloric acid and chlorides, occur in much smaller and more variable quantities. During thunderstorms oxides of nitrogen are formed, and these give rise to nitrous and nitric acid; ozone is also probably produced under such circumstances. The ammonia, carbon (soot), and sulphur compounds occur in larger quantity in the vicinity of towns, from the combustion of coal, or where decaying refuse is found. The hydrochloric acid and chlorides come for the most part from manufacturing operations, though it is significant that, especially during high wind, the air in the neighbourhood of the sea contains much more sodium chloride than is usual.

The relation of animal and plant life to air.—By breathing on a cool glass surface, and by expelling air from the lungs through lime-water, it is easy to demonstrate that expired air contains large quantities of moisture and carbon dioxide. Indeed the expired air from man contains usually over 4 per cent. of carbon dioxide, that is, over one hundred times as much as normal air.

The agencies at work in producing carbon dioxide are—

(1) Respiration of animals and plants.
(2) Combustion of fuel.
(3) Decay of organic matter.
(4) Subterranean causes.

Faraday calculated that nearly five million tons of carbon dioxide were contributed daily to the atmosphere by these processes. Under such a contribution the air would slowly get more and more charged with carbon dioxide, and the percentage of oxygen diminish.

There are, however, processes constantly in operation which act in the opposite direction.

(1) In the process of assimilation the green colouring matter of plants (chlorophyll), in presence of direct or diffused sunlight, effects the decomposition of carbon dioxide and liberates oxygen.

(2) Carbon dioxide being moderately soluble in water is carried down by rain, and is also taken up by surface waters and sea water.

The precise extent to which the loss and gain counteract one another is difficult to estimate, but that plant life is an important factor is shown by actual observations on the living plant, and by the variations in the amount of carbon dioxide in air in the neighbourhood of forests in the daytime, when the foliage is exposed to the sun's rays, as compared with night, when assimilation is checked and only respiration goes on.

Is air a compound or a mixture of nitrogen and oxygen?—We have seen that a chemical compound shows the following characters—

(1) It possesses a *definite* composition (see p. 21).

(2) The weights of the elements composing it are in proportion to the atomic weights, or in some simple multiple proportion of the atomic weights—*e. g.* HgI, HgI_2, H_2O, etc. (see p. 22).

(3) The compound shows distinctive physical and chemical properties, the individual properties of the constituent elements being more or less completely concealed (see p. 14).

(4) When combination takes place, heat is usually evolved (see p. 18).

(5) When gases combine to form a gaseous compound there is always a condensation to *two volumes,* whatever the volumes of the constituent gases may be, thus—

2 vols. hydrogen + 1 vol. of oxygen form 2 vols. water vapour.
3 „ „ + 1 „ nitrogen „ „ ammonia.
(See p. 59.)

(6) The simple solution of a gas in water does not affect its

chemical composition; for instance, if we dissolve ammonia or carbon dioxide in water, and then, by boiling the solution, expel the gas again, it will be found to be unaltered in character or composition.

Now let us apply these tests to air.

(1) The composition of air varies very little under different circumstances, but even such small variations as are found in its composition do not occur in the case of chemical compounds.

(2) If we divide the relative proportions by weight of nitrogen and oxygen in the air by the atomic weights of nitrogen and oxygen, we shall see whether any simple multiple relation is shown.

$$\text{Nitrogen } \frac{76{\cdot}995}{14} = 5{\cdot}499;$$

$$\text{Oxygen } \frac{23{\cdot}005}{15{\cdot}96} = 1{\cdot}441;$$

$$\text{And } 5{\cdot}499 : 1{\cdot}441 :: 3{\cdot}82 : 1.$$

That is, to be even approximately in agreement with the results of analysis we should have to assume a compound $N_{19}O_5$. The same result may be arrived at by considering the volume relations of nitrogen and oxygen in air.

(3), (4), and (5) Nitrogen and oxygen retain their characters with slight modification in air, and a mixture of the two gases in the proper proportions shows precisely the same characters in all respects as air. No heat is evolved when they are brought together, nor does any contraction in volume take place.

(6) When air is shaken up with water, a greater proportion of oxygen dissolves than nitrogen, owing to the greater degree of solubility of oxygen, so that whilst in the air originally taken, one volume of oxygen is associated with approximately four volumes of nitrogen, air dissolved in water consists of one volume of oxygen associated with two volumes of nitrogen.

On all these grounds, therefore, we must admit that air is simply a *mixture* of nitrogen and oxygen.

Fogs are caused by condensation of water vapour induced by dust. That dust is the cause of fog formation is proved by the fact that in filtered air, fogs do not form. Analysis of the deposit left after a fog showed it to consist of carbon, hydrocarbons, sulphuric acid, iron and its oxides, and silica. During a fog, too, the amount of carbon dioxide increases enormously and reaches from three to five times the normal amount.

AMMONIA, NH_3.—Ammonia or its compounds exist in small quantities in air and in natural waters, being produced either from oxides of nitrogen formed in the air, or by the action of bacteria from refuse matters in the soil. Whenever animal or vegetable products containing nitrogen are strongly heated in closed retorts (air being excluded), and especially when they are heated with lime or other alkalies, ammonia is given off.

In this way large quantities of ammonia are obtained during the distillation of coal (which contains about 1½ per cent. of nitrogen), the coal gas being cooled and then washed, by which means any ammonia is separated and obtained in solution. The further distillation of the liquid so obtained with lime, sets free the ammonia, which if passed into aqueous hydrochloric acid, forms ammonium chloride or sal ammoniac.

$$NH_3 + HCl = \underset{\text{Ammonium chloride.}}{NH_4Cl.}$$

The distillation of animal refuse, horns, or hoofs with lime likewise affords ammonia, and "spirits of hartshorn" is a name by which a solution of ammonia is known.

Preparation.—In the laboratory it is usually prepared by heating together a mixture of two parts of lime and one part of ammonium chloride. Both must be in a state of fine powder, intimately mixed, and as dry as possible. The mixture is heated in a dry flask, and the gas collected over mercury or upward by displacement, being much lighter than air; it cannot be collected over water owing to its very great solubility. If it is to be dried, the ordinary desiccating agents for gases cannot be used, since sulphuric acid combines with it with great readiness, and calcium chloride absorbs it; a layer of lime or fragments of caustic soda may, however, be used.

Properties.—Ammonia is a colourless gas, having a very pungent but not disagreeable odour if diluted with much air; in the pure condition it is injurious when breathed in quantity.

At −34° C. at ordinary pressure, and at 0° C. under a pressure of seven atmospheres, dry ammonia condenses to the liquid form.

Exp. 76.—Fill a litre flask by displacement with dry ammonia, and show its solubility in the same way as already described (p. 42).

Water at 0° C. dissolves 1,050 times its volume of the gas, and at 15° C. 727 volumes. The aqueous solution is lighter than water, and in its most concentrated form has the specific gravity 0·884; it contains 36 per cent. by weight of the gas. The gas may be entirely expelled by boiling the solution.

Ammonia neither burns readily in air nor supports combustion, but a mixture of warm ammonia and oxygen burns with a greenish-yellow flame.

Exp. 77.—Gently warm a strong solution of ammonia in a wide-mouthed eight-ounce flask, and bubble oxygen gas through the solution at the same time. A mixture of ammonia and oxygen will pass out at the open mouth of the flask, and will burn when a light is applied to it.

Metallic oxides which are reduced in hydrogen also undergo reduction when heated in ammonia gas, and in most cases the hydrogen of the ammonia combines with the oxygen of the oxide to form water, and nitrogen is set free.

Ammonia combines directly with acids to form ammonium salts; this can be well shown with hydrochloric acid gas.

Exp. 78.—Fill two similar jars by displacement with ammonia and hydrochloric acid gas respectively, and cover the mouth of each jar with a glass plate. Now bring them mouth to mouth and withdraw the glass plates. The gases as they come into contact will combine, forming a fine white powder, which remains for some time diffused throughout the jars. This body is ammonium chloride, NH_4Cl.

$$\underset{\text{2 vols.}}{NH_3} + \underset{\text{2 vols.}}{HCl} = NH_4Cl.$$

Ammonium sulphate, $(NH_4)_2SO_4$, ammonium nitrate, NH_4NO_3, and other salts may be obtained by neutralizing a solution of ammonia with the respective acids, and then evaporating to dryness on a water-bath.

SUMMARY.

(1) Nitrogen occurs naturally in the free state in the atmosphere.
„ „ „ in combination in animal and vegetable tissue, in coal, nitrate of soda and ammonia.

(2) *Preparation*—
- (*a*) from air by abstraction of oxygen,
- (*b*) by heating ammonium nitrite,
- (*c*) by the action of chlorine on ammonia.

(3) *Properties.*—
- (*a*) Very slightly soluble in water.
- (*b*) Extremely difficult to liquefy.
- (*c*) Chemically inert, yet it combines directly with some few elements but not readily.

(4) *The Atmosphere.*—

Essential constituents are Nitrogen and Oxygen associated with CO_2, and moisture.

Contributions of CO_2 (and moisture) are constantly made by animal and plant life and by the combustion of fuel, also other gases in minute quantities.

Moisture undergoes partial removal in the form of rain.

Carbon dioxide undergoes partial removal by plants and by solution in water.

(5) Composition and behaviour of air as indications that its constituents are merely mixed together and not chemically combined.

Ammonia.

(6) *Preparation.*—

By distillation of (*a*) ammonia salts (*b*) nitrogenous animal or vegetable substances, with caustic alkalies.

(7) *Properties.*—
- (*a*) Great solubility in water.
- (*b*) Liquefied under moderate pressure and cold.
- (*c*) Lighter than air, characteristic odour.
- (*d*) Non-supporter of combustion, combustible under certain circumstances.
- (*e*) Combines with acids forming salts.

QUESTIONS.—CHAPTER XIII.

1. Describe a method by which nitrogen may be obtained from air by removal of oxygen.
2. Give two methods for the preparation of nitrogen from ammonia or ammonium salts.
3. State the chief physical and chemical properties of nitrogen.
4. A mixture of 25 c.c. of air and 50 c.c. of hydrogen is exploded in a eudiometer, and the volume of the residual gas is found to be 60·3 c.c.; find the percentage of oxygen in the air.
5. A litre of dry air is passed over heated copper and the increase in the weight of the copper found to be 0·297 gramme, find the percentage by weight of oxygen in the air. (1 litre of air weighs 1·293 grammes.)
6. How do the following impurities originate in air:—carbon dioxide, ammonia, sulphurous acid?
7. What agencies are at work which tend to remove such impurities as carbon dioxide and ammonia from the air?
8. In what respects does a *mixture* of two gases, such as nitrogen and oxygen, differ in its behaviour from a *compound* of the two gases when shaken up in contact with water?
9. What indications are usually shown that two gases which you have brought together have entered into combination?
10. Give a general method by which ammonia may be obtained from nitrogenous animal or vegetable substances.
11. How would you prepare and collect dry ammonia?
12. How can it be shown that ammonia contains hydrogen?

CHAPTER XIV.

OXIDES AND OXY-ACIDS OF NITROGEN.

In the following table is given a list of these compounds—

Nitrous oxide, N_2O.	Hyponitrous acid, HNO.
Nitric oxide, NO.	
Nitrogen trioxide, N_2O_3, or nitrous anhydride.	Nitrous acid, HNO_2.
Nitrogen peroxide, N_2O_4.	
Nitrogen pentoxide, N_2O_5, or nitric anhydride.	Nitric acid, HNO_3.

Occurrence.—The higher oxides are formed in small quantity when the electric discharge takes place in a mixture of nitrogen and oxygen. These oxides, or nitrous and nitric acid formed from them, therefore occur in the atmosphere and in rain water; waters contaminated by the drainage of surface soil, or by decaying nitrogenous organic matter, also contain similar products. In all such cases, owing to the difficulty of bringing about direct combination of nitrogen and oxygen, they are present in very minute quantities. Nitric acid or the nitrates being in all cases the source from which the oxides of nitrogen are derived, we shall treat these first.

NITRIC ACID, HNO_3. *Preparation.*—Nitric acid, being a volatile acid, is expelled from nitrates by the action of less volatile acids, such as concentrated sulphuric acid (or silica), and this reaction is made use of in its preparation, nitrate of potash or soda being usually employed.

Exp. 79.—Introduce 20 grammes of potassium nitrate into a stoppered retort, and as much concentrated sulphuric acid as will just cover it. Apply a moderate heat, and presently the vapour of nitric acid will pass over and condense in the neck of the retort. The liquid may be collected in a small flask slipped over the mouth of the retort, and kept cool by means of a stream of cold water, or a wet cloth. When about 10 c.c. have been distilled over, or so soon as whitish fumes of sulphuric acid begin to appear, the experiment should be stopped.

$$\underset{\text{Potassium nitrate.}}{KNO_3} + H_2SO_4 = \underset{\text{Acid potassium sulphate.}}{KHSO_4} + HNO_3.$$

On the large scale, the native Chili saltpetre, $NaNO_3$, is employed, being a cheaper material, and the distillation is performed in large iron cylinders, the condensation of the acid taking place in a series of stoneware bottles, as shown in figure 27.

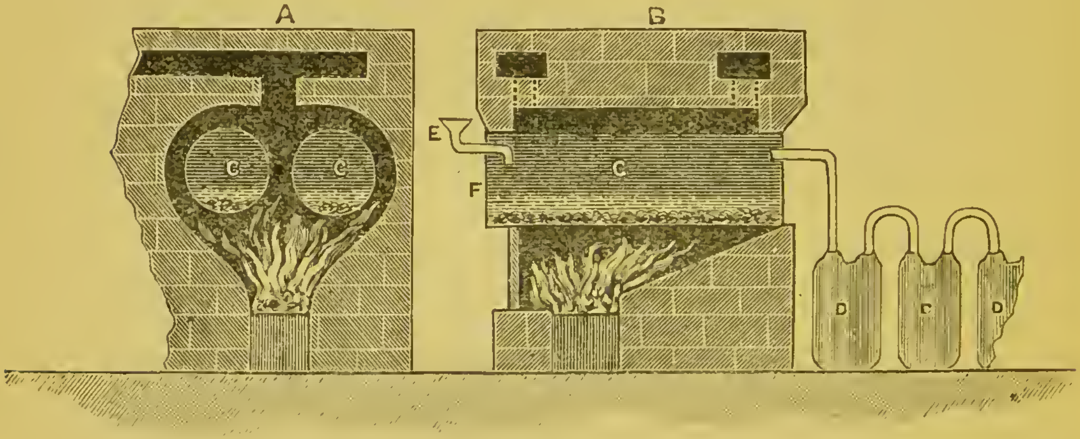

FIG. 27.

Economy can also be effected in regard to the amount of sulphuric acid used, since it is practicable to work at a temperature sufficiently high to leave as the residue the normal sulphate of sodium, and hence the reaction is—

$$\underset{\text{Sodium nitrate.}}{2\,NaNO_3} + H_2SO_4 = \underset{\text{Sodium sulphate}}{Na_2SO_4} + 2\,HNO_3.$$

Properties of the acid.—The pure acid is a colourless, fuming liquid, of specific gravity 1·53, boiling at 86° C. It is highly corrosive, and by contact, instantly stains the skin yellow, more prolonged exposure giving rise to serious wounds. Dry straw and woody fibre are charred or even set fire to by contact with it. It mixes with water in all proportions, and if the dilute solution be concentrated in air at atmospheric pressure it becomes stronger until 68 per cent. of acid is present; it then distils unchanged.

It is chiefly characterized by its powerful oxidizing action, carbon, sulphur, and tin being transformed readily into CO_2, H_2SO_4, and SnO_2 respectively; whilst turpentine, when mixed with it, inflames. When it is remembered how readily nitric acid breaks up (*e. g.* by passing its vapour through a red-hot tube) into water, oxides of nitrogen, and oxygen, the powerful oxidizing action of nitric acid will be understood.

Most metals are dissolved by it with the evolution of red fumes, the nitrate of the metal, or, in some cases, the oxide being formed. The reactions which take place are complex, and vary according to the conditions under which the experiment is performed and the strength of the acid used. The more important examples are expressed by the equations below—

$$\begin{array}{rcllll} Sn & + & 4\,HNO_3 & = SnO_2 & + 2\,N_2O_4 & + 2\,H_2O. \\ 4\,Ag & + & 6\,HNO_3 & = 4\,AgNO_3 & + N_2O_3 & + 3\,H_2O. \\ 3\,Cu & + & 8\,HNO_3 & = 3\,Cu(NO_3)_2 & + 2\,NO & + 4\,H_2O. \\ 4\,Zn & + & 10\,HNO_3 & = 4\,Zn(NO_3)_2 & + N_2O & + 5\,H_2O \end{array}$$

Regarding nitric acid as composed of water (H_2O) and nitric anhydride (N_2O_5), we see that with the different metals in the order taken, the extent of the reduction of the N_2O_5 increases; thus—

$$\begin{array}{llll} Sn & \text{reduces } 2\,N_2O_5 \text{ to } 2\,N_2O_4 & \text{and forms} & SnO_2 \\ 4\,Ag & ,,\quad N_2O_5 \text{ to } N_2O_3 & ,,\quad ,, & 2\,Ag_2O. \\ 3\,Cu & ,,\quad N_2O_5 \text{ to } N_2O_2\,(2\,NO) & ,,\quad ,, & 3\,CuO. \\ 4\,Zn & ,,\quad N_2O_5 \text{ to } N_2O & ,,\quad ,, & 4\,ZnO. \end{array}$$

The three last oxides combine with sufficient N_2O_5 to form nitrates, the water being eliminated.

The so-called "noble" metals, such as gold and platinum, are not acted upon by it, but readily dissolve in a mixture of hydrochloric and nitric acids,[1] which has for this reason been termed *aqua regia.*

---

[1] *Aqua regia* is usually made by mixing nitric acid with four times its volume of hydrochloric acid.

Exp. 80.—To a few cubic centimetres of *dilute* nitric acid in a porcelain basin add fragments of lead, digesting on a water-bath, until the acid is saturated, and no more of the metal will dissolve. Evaporate the clear liquid to dryness, and a white salt, nitrate of lead, remains.

Exp. 81.—Dilute 5 c.c. of nitric acid with an equal bulk of water, and add a little litmus solution, which will become of a bright red colour. Now add ammonia solution little by little until the last drop turns the litmus blue, and concentrate the liquid to a point at which, when a drop of it is allowed to cool on the end of a glass rod, it crystallizes. On standing, crystals of ammonium nitrate will be obtained.

The nitrates.—These salts may be looked upon as nitric acid in which the hydrogen of the acid is replaced by a metal, thus—

$$\mathrm{HNO_3} \qquad \mathrm{KNO_3} \qquad \mathrm{NaNO_3} \qquad \mathrm{NH_4NO_3} \qquad \mathrm{AgNO_3}.$$

$$\left.\begin{matrix}\mathrm{HNO_3}\\ \mathrm{HNO_3}\end{matrix}\right\} \quad \mathrm{Pb(NO_3)_2} \qquad \mathrm{Cu(NO_3)_2} \qquad \mathrm{Ca(NO_3)_2} \qquad \mathrm{Ba(NO_3)_2}.$$

They are all soluble in water. The nitrates of the alkalies are the most stable, and those of the heavy metals the least stable. When strongly heated, all undergo decomposition with the evolution of nitric acid or the products of decomposition of nitric acid, viz. oxides of nitrogen and oxygen, and exert a powerful oxidizing action on substances which may be mixed with them.

Exp. 82.—Heat a few grammes of potassium nitrate in a test-tube until it fuses, and then drop into it one or two fragments of dry charcoal. The charcoal will ignite and burn with violence, being oxidized by the nitrate to CO_2.

Exp. 83.—Repeat the experiment, introducing a few small shavings of lead; the lead will be oxidized at the expense of the nitrate and transformed into a yellowish powder of oxide of lead.

Tests for nitrates.—(1) Nitrates when heated with sulphuric acid or silica give off nitric acid fumes, often accompanied by red fumes of the higher oxides of nitrogen.

(2) Mix a solution of a nitrate with strong sulphuric acid, and add copper turnings; on warming, red fumes will be given off.

(3) (The most sensitive test). Mix a cold solution of a nitrate with a cold, strong solution of ferrous sulphate, and pour gently down the side of the tube strong sulphuric acid: the latter sinks

to the bottom, and a dark ring forms above it. The sulphuric acid liberates nitric acid from the nitrate, and the ferrous sulphate reduces the nitric acid to nitric oxide, which combines with more ferrous sulphate to form the dark-coloured solution.

NITROUS OXIDE, N_2O.—This gas is familiarly known as "laughing gas," because when breathed in small quantity it produces a feeling of exhilaration. Inhaled in larger quantities it is an anæsthetic, and renders the subject insensible to pain, and is for this reason employed in dentistry.

Preparation.—It has already been pointed out (p. 151) that when nitric acid (dilute) is acted upon by zinc, nitrous oxide is formed. It is more usual, however, to prepare it by heating ammonium nitrate, the decomposition being represented by the equation,

$$NH_4NO_3 = N_2O + 2\ H_2O.$$

Introduce about 30 grammes of dry ammonium nitrate into a 4-ounce flask and heat gently, and just so as to bring about a steady and not too rapid evolution of the gas. The delivery-tube should be wider than usual, as the salt is liable to be carried over and stop up the tube; also stop the experiment when about two-thirds of the salt has been decomposed or an explosion may ensue. Cold water dissolves about its own volume of the gas; it may, however, be collected over hot water.

Properties of nitrous oxide.—It is a colourless gas with an agreeable odour and taste. It condenses at 15° C. under a pressure of 40 atmospheres to a liquid which boils at $-92°$ C. under ordinary pressure. One hundred volumes of water dissolve 130 volumes of the gas at 0° C., 92 at 10° C., and 67 at 20° C.

It is easily decomposed by heat, and supports combustion as readily as oxygen.

Exp. 84.—Plunge a glowing taper into a jar of nitrous oxide, and it will burst into a flame just as it does in oxygen. Sulphur and phosphorus also burn in the gas with almost as much vigour as in oxygen, though if only feebly ignited they may be extinguished. To distinguish it from oxygen, pass nitric oxide into a jar of the gas—no red fumes will appear.

NITRIC OXIDE, NO. *Preparation.*—A few grammes of copper turnings are introduced into an 8-ounce flask provided with a thistle funnel and delivery-tube, and about 50 c.c. of a mixture of equal parts of nitric acid and water. In a few moments gas begins to be evolved without the application of heat, and red fumes appear in the flask.

These red fumes are formed by the action of the nitric oxide on the oxygen contained in the flask; after a time the colour disappears as they are displaced, and the gas may then be collected. The reaction which takes place is—

$$3\ Cu + 8\ HNO_3 = 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O;$$

essentially it is

$$3\ Cu + 2\ HNO_3 = 3\ CuO + 2\ NO + H_2O,$$

and the CuO with the excess of nitric acid becomes $Cu(NO_3)_2$.

The gas is not very soluble in water (water dissolves about $\frac{1}{20}$th its volume under ordinary conditions), and it may be collected over water. It dissolves in a cold solution of ferrous sulphate (as $FeSO_4.NO$), and is expelled in a very pure condition from such a solution on warming it.

Properties of nitric oxide.—It is a colourless gas which by mere admixture combines with oxygen, giving rise to red fumes of the higher oxides of nitrogen.

$$2\ NO + O_2 = N_2O_4.$$

It is very difficult to liquefy, requiring a pressure of 104 atmospheres at $-11°$ C.; the liquid boils at $-93°$ C. It is a tolerably stable body, and is only decomposed at a red heat.

Exp. 85.—Expose a jar of the gas to air, and observe the red fumes.

Exp. 86.—Pass oxygen into a jar of the gas standing over water little by little, allowing an interval to elapse between each addition. Red fumes will be formed, and these will dissolve in the water, which gradually rises in the jar. If the gas be pure and the oxygen be added in the proper proportion, the water will rise to completely fill the jar. A dilute solution of nitrous acid is thus formed, and may be shown to liberate iodine from potassium iodide, or to decolourize permanganate of potash.

Exp. 87.—The flame of phosphorus, if feebly burning, will be extinguished in the gas, whilst if already fully ignited it will continue to burn brightly. The temperature at which the gas is decomposed being about 600° C., this seems to indicate that combustion is only supported when the temperature is sufficient to decompose the gas, the oxygen which is liberated being the supporter of the combustion.

SUMMARY.

Nitric acid.

- (1) *Preparation.—*
  - From nitrates by heating with sulphuric acid.
- (2) *Properties.—*
  - (*a*) Fuming corrosive liquid.
  - (*b*) Powerful oxidizing agent.
  - (*c*) Dissolves many metals forming nitrates and evolving one or other of the oxides of nitrogen.
  - (*d*) Nature of *aqua regia*.
- (3) *Nitrates.—*
  - (*a*) All soluble in water.
  - (*b*) Mostly unstable at high temperatures.
  - (*e*) Oxidizing agents at high temperatures.
  - (*d*) Characteristic tests.

Nitrous oxide.

- (1) *Preparation.—*
  - (*a*) by heating ammonium nitrate.
  - (*b*) by the action of zinc on dilute nitric acid.
- (2) *Properties.—*
  - (*a*) Moderately soluble in water.
  - (*b*) Liquefied under moderately high pressure.
  - (*e*) Supports combustion as readily as oxygen.
  - (*d*) Forms no red fumes when mixed with nitric oxide.
  - (*e*) Effect of breathing the gas.

Nitric oxide.

- (1) *Preparation.—*
  - By the action of nitric acid on metallic copper.
- (2) *Properties.—*
  - (*a*) Only slightly soluble in water.
  - (*b*) Readily soluble in a cold solution of ferrous sulphate.
  - (*c*) Liquefied under very high pressure and cold.
  - (*d*) Combines readily with oxygen forming higher oxides of nitrogen.
  - (*e*) Supports combustion under certain conditions.

QUESTIONS.—CHAPTER XIV.

1. How do you account for the occurrence of oxides of nitrogen, and the oxy-acids or salts of these, in the air and in the soil?
2. How is nitric acid prepared on the large scale?
3. In what respects does nitric acid differ from sulphuric acid?
4. Give striking experiments calculated to illustrate in regard to nitric acid, (*a*) its powerful oxidizing action;
   (*b*) „ „ solvent action.
5. How would you prepare nitrates of lead and potassium, and obtain them in the form of crystals?
6. By what chemical reactions may nitrates be recognized?
7. Express by means of equations the action of copper, cupric oxide, lead oxide, and tin respectively on nitric acid.
8. What are the properties of nitric oxide, and how may it be distinguished from nitrous oxide?
9. Give two methods for the preparation of nitrous oxide.
10. State the *physical* properties of nitrous oxide, and say how you would distinguish by chemical tests nitrous oxide from oxygen. In what respects does it resemble oxygen?

CHAPTER XV.

CARBON.

CARBON is the first member of a group consisting of the elements carbon, silicon, titanium, zirconium, and thorium, of which the first two members alone come under consideration amongst the non-metals. They show a considerable resemblance to one another in their physical and chemical properties.

Comparing together more particularly carbon and silicon we observe that—

(1) The elements themselves are very infusible.

(2) They exist in allotropic modifications of similar character.

(3) They form oxides of great stability and also gaseous hydrides, CH_4 and SiH_4, the former of these being a stable body, whilst the latter undergoes decomposition very readily.

(4) Carbon and silicon both combine directly with fluorine to form CF_4 and SiF_4 respectively. With the other halogen elements they do not combine directly, but volatile liquid tetrachlorides CCl_4 and $SiCl_4$ are obtained indirectly.

Occurrence.—Carbon is found in nature in a state of comparative purity as diamond and graphite, the latter known as mineral plumbago, from which black-lead pencils are made. These forms do not, however, occur in any very considerable quantity, and the sources from which the large supplies of carbon are obtained are coal and vegetable matter.

The tissue of plants is very constant in composition, and disregarding the moisture and the mineral ash left after combustion, amounting usually to about 1 per cent., *dried wood* is found to consist of

Carbon	50 per cent.
Hydrogen	6 ,,
Oxygen and nitrogen	44 ,,

Where plants undergo decay and form thick accumulations of *peat*, the relative proportion of the carbon increases, and the following may be taken as the average composition of peat, leaving out of account moisture and mineral matter—

Carbon	58 per cent.
Hydrogen	5 ,,
Oxygen and nitrogen	37 ,,

In deposits of peat and the remains of vegetation which have lain for long periods of time this process of parting with the more volatile constituents and consequent increase in the proportion of carbon goes on, and instead of peat we have a much denser product known as *brown coal* or *lignite*, in which the structure of the vegetation composing it can, however, still be observed. Lignite varies greatly in composition, especially in regard to the amount of moisture and ash. Excluding these, it contains on the average—

Carbon	66 per cent.
Hydrogen	5 ,,
Oxygen and nitrogen	29 ,,

In the older formations of the earth's crust there are large deposits of *coal*, which have resulted from long-continued action similar to the foregoing. The seams of coal usually occur at some depth, and are overlaid by other strata. The vegetable tissue from which coal is derived has thus been subjected to immense pressure and to increased temperature, and under these agencies, acting over long periods of time, the changes already noticed in the passage from woody tissue to lignite have been still further accentuated. Coal is darker in colour, denser, and more brittle; as to composition, the following numbers may be compared with those given for wood, peat, and lignite—

	Bituminous Coal.	Anthracite.
Carbon	84 per cent.	94 per cent.
Hydrogen	5 ,,	3 ,,
Oxygen and nitrogen ...	11 ,,	3 ,,

Over 150 million tons of coal are brought to the surface in the United Kingdom annually. In many localities, especially in South Russia and the United States, there are large deposits of *petroleum*—a mixture of various oils, but all composed of carbon and hydrogen, and hence termed hydrocarbons.

And when we add the very extensive series of carbon compounds which have been prepared in the laboratory from coal tar and petroleum, and the products, such as starch, sugar, turpentine, albumen, stearin, etc., elaborated by plants and animals, we are in a position to appreciate the immense importance of the element carbon. The study of such bodies is indeed set apart as a special branch of the science, and known as *Organic Chemistry*, or the Chemistry of the Carbon Compounds.

Finally, carbon occurs in combination with oxygen as carbon dioxide in the air, and in vast deposits of limestone and dolomite. The carbon dioxide in air, being less than 4 volumes in 10,000, might be regarded as insignificant, but the mass of the atmosphere is such that at this computation there must be very nearly a billion tons of carbon in it.

Allotropic forms of carbon.—(1) *Diamond* is the crystalline form of carbon; it is found in South Africa and Brazil, usually as octahedra or cubes, or as some modifications of these. Its value is due to its great hardness and brilliancy of lustre, and to the fact that it does not oxidize or undergo change even in presence of corrosive substances. It is the densest form of carbon, having a specific gravity of about 3·5, and is also the most difficult to ignite in oxygen.

It is therefore not to be wondered at that the composition of diamond remained unknown until the time of Lavoisier, although it had been previously observed that diamond could be burnt and left no appreciable residue. Lavoisier about a century ago, by means of a burning glass, ignited diamond in air enclosed over mercury, and found that when it burnt, the gas which was formed turned lime-water milky and was carbon dioxide. Dumas, later, showed that carbon dioxide was the *only product* obtained when diamond is burnt in oxygen, and that every 12 parts by weight of diamond yielded 44 parts of carbon dioxide, according to the equation—

$$\begin{array}{ccccc} C & + & O_2 & = & CO \\ 12 & & 32 & & 44 \end{array}$$

Diamond consists therefore (with the exception of a minute quantity of ash) of pure carbon.

(2) *Graphite.*—This also occurs naturally, being found usually in the older crystalline rocks. Cast-iron contains plates of this form of carbon, which can be seen at a freshly-fractured surface, and masses of it accumulate at the base of blast furnaces. It is a soft, dark-grey substance, with a metallic lustre, and possesses a much lower specific gravity (2·2) than diamond. Graphite (and also amorphous carbon) is acted upon when gently heated with a mixture of potassium chlorate and nitric acid, whilst diamond is unattacked.

(3) *Amorphous carbon* is familiar to us as charcoal, lamp-black, or animal charcoal, which, however, are usually more or less impure forms of carbon. The former may be obtained by strongly heating wood or organic bodies in vessels from which air is excluded, or by the action of dehydrating substances such as concentrated sulphuric acid.

Exp. 88.—Heat a few pieces of wood in a hard glass tube over the flame of a Bunsen burner. Volatile vapours are at first given off and burn at the mouth of the tube, and when these are no longer to be seen, throw out the contents of the tube into water. The black charred product is wood charcoal, and though its specific gravity is 1·8 or thereabouts, it will float on water in consequence of the large amount of air contained within its pores. A special form of charcoal is manufactured by charring wood by means of superheated steam.

Exp. 89.—Make about 100 grammes of sugar into a thick syrup by dissolving it in a small quantity of hot water, and place it in a deep glass cylinder, then pour in about 100 c.c. of concentrated sulphuric acid. Presently the liquid will blacken and froth considerably, and a mass of black charcoal much more bulky than the sugar originally taken will be formed. Wash this thoroughly with water till free from acid, and there remains carbon in a granular, amorphous condition. By drying this, and then heating it in a stream of chlorine to remove hydrogen or other gases, a very pure specimen of carbon is obtained.

Animal charcoal is prepared by charring bones in closed iron retorts; it consists of a mixture of very porous charcoal and the mineral constituents of bone (chiefly phosphate of lime). It is used for decolourizing raw sugar, as it has the property of removing many colouring matters.

> **Exp. 90.**—Shake up with animal charcoal a hot solution of indigo or litmus for a few moments and then pour it on a filter, the filtrate will be colourless. That the colouring matter is removed by the animal charcoal and not by the filter, may be shown by pouring a similar solution which has not been treated by animal charcoal through a filter paper.

Lamp-black may be made by burning resin or turpentine, and bringing a cool surface, *e. g.* the under-side of a porcelain basin filled with cold water, into the flame. In this form, after treatment with chlorine, a particularly pure and finely-divided form of carbon is prepared.

In whatever form it occurs, carbon is infusible at the highest temperatures attainable; it is also a very bad conductor of heat or electricity. It cannot be considered an element of great chemical activity, since at ordinary or moderate temperatures it does not combine directly with any of the elements except fluorine, and even at high temperatures there are comparatively few elements with which it shows a disposition to unite directly. At high temperatures, however, it combines directly with oxygen, forming carbon monoxide or carbon dioxide; with sulphur to form carbon bisulphide, and with hydrogen to form acetylene (C_2H_2).

Two very characteristic properties are—(1) its power of absorbing gases manifested by the amorphous form; (2) its activity as a reducing agent. If by exposure to a vacuum the air be removed from the pores of wood charcoal, and this body be then introduced into an atmosphere of ammonia or carbon dioxide, etc., the volume of gas taken up will be many times greater than that of the charcoal. The gas therefore undergoes condensation, and some heat is evolved in consequence. Cocoanut charcoal, under favourable conditions, was found to absorb of

Ammonia ...	... 172	times	its	volume.
Hydrochloric acid	... 165	,,	,,	,,
Nitrous oxide	... 99	,,	,,	,,
Carbon dioxide	... 97	,,	,,	,,

It is this power of absorbing gases to which charcoal owes its efficacy as a medium for disinfecting purposes, the gaseous products of putrefaction being taken up within its pores: and gases like sulphuretted hydrogen are oxidized by absorbed oxygen.

We have already had an example of a *gaseous* reducing agent in hydrogen, which, owing to its affinity for oxygen, reduces many oxides to the metallic condition. And in sulphurous acid or phosphorous acid we have instances of *liquids* as reducing agents, their activity being due to the ease with which they undergo oxidation to sulphuric acid and phosphoric acid respectively. In carbon we have a *solid* reducing agent which finds very frequent employment in operations conducted at high temperatures, the carbon under such conditions being oxidized to carbon monoxide or dioxide at the expense of the oxygen contained in the bodies with which it is mixed.

Thus, most metallurgical operations involving a reduction of oxides to the metal, are carried out with the use of carbon in the form of coke or coal which is oxidized to CO or CO_2 in the process.

Exp. 91.—Make an intimate mixture of about a gramme of finely-powdered oxide of lead (litharge) with about one-tenth its weight of charcoal, and heat to redness in a hard glass tube or porcelain crucible for five minutes. Now throw some of the powder into a mortar with a little water and rub it up, using pressure, with the pestle, and then wash away the charcoal by means of a stream of water. Pellets or plates of metallic lead will be obtained—

$$2\,PbO + C = 2\,Pb + CO_2$$

Similarly, oxide of copper or bismuth may be reduced, and metallic copper or bismuth obtained from them.

The reduction of iron ores, or oxide of zinc or tin, are examples of similar reductions carried out on the large scale.

SUMMARY.

(1) *Carbon* occurs in free state as diamond and graphite, and forms also an essential constituent of animal and vegetable organisms and of carbonaceous matter (coal, etc.) resulting therefrom; also in the carbon dioxide of the atmosphere and the carbonates found either as minerals or rock-masses (limestone, etc.)

(2) *Allotropic forms.*—
  (*a*) Crystals of the regular system—*diamond,* sp. gr. 3·5.
  (*b*) Vitreous masses, sometimes crystallized in the hexagonal system—*graphite,* sp. gr. 2·2.
  (*c*) Amorphous—*charcoal* or lampblack.

(3) *Properties.*—
  (*a*) Infusible at the highest temperature of the furnace.
  (*b*) In the amorphous condition it occludes gases.
  (*c*) Reducing agent.
  (*d*) Combines directly with oxygen, sulphur and hydrogen at high temperatures.

QUESTIONS.—CHAPTER XV.

1 Show in tabular form the percentage of carbon and hydrogen in (*a*) wood, (*b*) peat, (*c*) lignite, (*d*) bituminous coal, (*e*) anthracite.

2. Taking the atmospheric pressure as 15 lbs. on the square inch, calculate the weight of carbon in a column of the air whose base is a square mile, the carbon dioxide present being 0·06 per cent. by weight of the air.

3. What are the properties characteristic of carbon?

4. How may it be shown that sugar contains carbon?

5. Compare the densities of diamond, graphite, and amorphous carbon. What do you regard as a full and sufficient proof that each of these bodies consists of the same element?

6. What is animal charcoal, and how is it prepared?

7. How would you show that charcoal takes up gaseous ammonia when exposed in an atmosphere of that gas?

8. What application is made of this property of absorbing gases which is shown in so marked a manner by charcoal?

9. State the conditions under which carbon monoxide is formed when oxygen is passed over carbon. What is the effect of passing steam over white-hot carbon?

10. What is a reducing agent? Give examples of solid liquid and gaseous reducing agents, illustrating your answer by equations showing the chemical changes which take place during reduction.

CHAPTER XVI.

FUELS—COMBUSTION.

WHENEVER carbon, hydrogen, or bodies containing carbon and hydrogen burn, they combine with the oxygen of the air, the carbon to form carbon monoxide or dioxide, and the hydrogen to form water, and the amount of heat accompanying the change is perfectly definite and constant.

If a gramme of pure carbon be burnt to carbon dioxide, the heat given out will be sufficient to raise the temperature of 8,080 c.c. of water one degree Centigrade. The heat requisite to raise one gramme (*i.e.* 1 c.c.) of water one degree Centigrade being adopted as the unit for measurement of heat (the calorie or thermal unit), we say that the heat of combustion of one gramme of carbon is 8,080 thermal units. So, in like manner, the combustion of a gramme of hydrogen is found to give rise to the evolution of 34,200 thermal units of heat. Hydrogen, therefore, on combustion gives out more than four times the amount of heat as compared with the same weight of carbon.

Bituminous coal consists chiefly of carbon, but as it contains some hydrogen, it should give out more heat on combustion than the same weight of carbon, and it would do so except that it contains usually 15 to 20 per cent. of oxygen, sulphur, nitrogen, and mineral ash, which are practically unproductive of heat. In anthracite, however, these constituents amount to little more than 5 per cent., and the heat of combustion of this kind of coal is greater than that of bituminous coal.

Petroleum, consisting entirely of carbon and hydrogen, and containing much more hydrogen than coal, actually does give out more heat than the same weight of carbon.

Fuel being employed for heating purposes, the amount of heat generated in its combustion is of primary importance, and the following table shows at a glance the comparative value of different substances which are applicable as fuels—

Hydrogen ...	34,200	thermal units	per gramme consumed.
Petroleum ...	12,000	„	„
Coal ...	7,500 to 8,500	„	„
Carbon ...	8,080	„	„
Wood ...	about 3,000	„	„

Flame.—Whenever a gas or vapour is brought into an atmosphere with which it can react chemically, and the heat generated is sufficient to bring about incandescence of the particles, flame is produced. The heat is generated and the incandescence effected in the region where the reaction is carried on, that is, at the surface where contact occurs between the two gases, as is seen when a jar of hydrogen burns mouth downwards. When we speak of hydrogen or coal gas as being combustible gases, and of air as being the supporter of combustion, we imply that hydrogen or coal gas, when once ignited, burn in air. And in flames under ordinary circumstances this is the case; if, however, we were to lead a stream of air from a jet into an atmosphere of coal gas, the flame would attach itself to the jet, and might be described as air burning in coal gas. In either case the flame marks the surface of contact between the air and coal gas, and is the region where the chemical changes take place which transform the hydrogen and carbon in the coal gas into water and carbon dioxide as ultimate products.

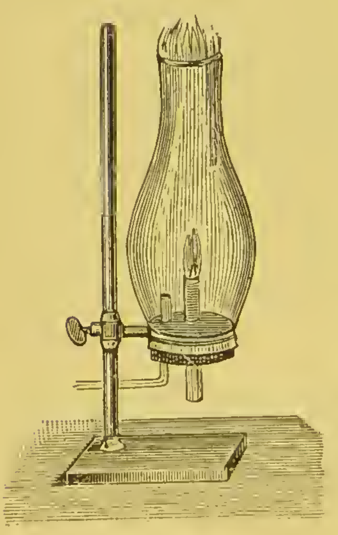
FIG. 28.

Exp. 92.—Fit into an ordinary lamp chimney a cork through which passes a short piece of straight wide tubing, and a second narrow piece bent at right angles as shown in Fig. 28, and connected with the supply of coal gas. Close the aperture at the top of the chimney, and allow the gas to escape by the straight tube until the air is displaced, then light it at the lower extremity of this tube and uncover the aperture at the top of the chimney. The flame will then pass up the tube and attach itself to the inner opening where the air and coal gas meet, the flame area being air and the surrounding atmosphere coal gas. The gas escaping at the top of the chimney may also be ignited, combustion occurring here in the ordinary manner.

Where the gases are intimately mixed and then ignited, the burning takes place with great rapidity, and explosion of a more or less violent nature ensues, but where a regular supply of the combustible product impinges upon the atmosphere in which it burns, a more or less steady flame is the result, the particular form of which is determined by the nature of the jet and the shaping influence of air-currents.

In any case before flame can be produced at all, the temperature of the combustible body must first reach a certain limit known as the *point of ignition*. This temperature varies with different bodies; the vapour of carbon bisulphide may be ignited by a glass rod heated only to 150° C., whilst with hydrogen or coal gas a dull red heat (600° C.) is insufficient. Conversely, a flame is extinguished if its temperature is by any means reduced below the point of ignition of the vapours consumed in it (see Exp. 97).

Exp. 93.—Hold a piece of wire gauze (about 30 meshes to the inch) horizontally over a Bunsen burner and about an inch above the orifice (Fig. 29). Turn on the gas and light it on the upper side of the gauze, the flame will not be communicated to the stream of gas on the under-side of the gauze. Much heat is carried off by the gauze, and the part of the flame in contact with the gauze where it meets the upward current of gas, is so far cooled in consequence of this that its temperature falls below the point of ignition of the gas.

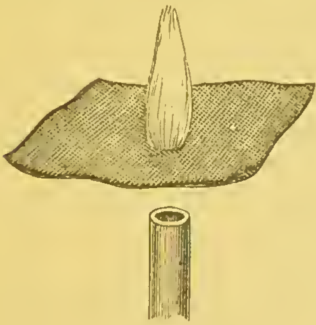

Fig. 29.

Exp. 94.—Make a piece of the wire gauze into a cylindrical roll and place a candle within it. Now direct the flame of a Bunsen burner against the outer surface of the gauze; the wax may be melted, but the candle

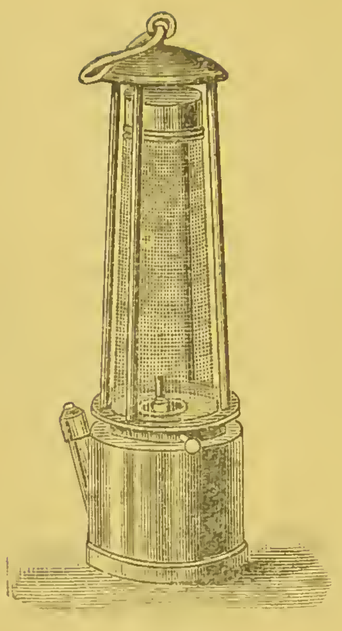

FIG. 30.

cannot be lighted unless the gauze is heated to redness. The reason for this will be gathered from the explanation given in the previous experiment.

The *Davy Lamp* (Fig. 30) is such an arrangement, in which an oil lamp is shut in by a layer of gauze, and even if such a lamp be entirely surrounded with inflammable gas, this will not become ignited, although the inflammable gas which passes through the gauze may burn inside it and fill the space above the oil lamp with flame. If, however, the gauze becomes strongly heated, or if the flame should be mechanically driven through the meshes, communication with the inflammable atmosphere outside may be established and ignition will then take place.

The candle flame.—The inflammable matter in a candle is the wax or tallow, consisting essentially of carbon and hydrogen. This is melted round the wick, which becomes charged and serves as a still from which the vapours of hydrocarbons are supplied into the area immediately surrounding it. That such an area exists containing combustible vapours may easily be shown.

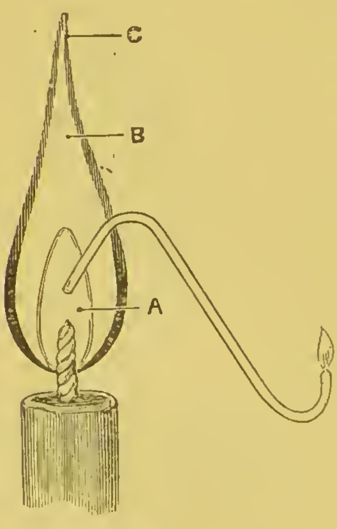

FIG. 31.

Exp. 95.—Depress a sheet of stout paper quickly into a candle flame to the level of the top of the wick, and hold it steadily there for about a second. On withdrawing it, a ring of sooty deposit will be seen, and within it a clear space. Secondly, take a glass syphon tube, as shown in Fig. 31, and bring the shorter limb into the centre of the flame; presently yellowish-brown vapours will be seen to pass down the tube and issue at the other end. These vapours will be found to be inflammable, and may be burnt at the exit of the tube.

We can thus distinguish in the candle flame—

(1) A central zone surrounding the wick and containing hydrocarbon vapours—the zone of no combustion (A in Fig. 31).

(2) A luminous zone or mantle surrounding the dark central zone, in which the hydrocarbons are in the process of combustion. The light emitted by the candle proceeds from this mantle, which contains white-hot particles of carbon and the products of the incomplete combustion of the hydrocarbon vapours (B C in Fig. 31). There is also, external to this,

(3) A non-luminous zone in which more intimate contact with the air is effected and the combustion is completed, the products formed consisting of carbon dioxide and aqueous vapour. Under ordinary circumstances this zone is not easily seen, but by sprinkling a little finely-powdered common salt over the flame it will flash out as a golden-yellow fringe, the colour of which is due to the salt.

The operations which take place in the three zones may be summed up in the order of their occurrence as (1) the vapourization of hydrocarbons, (2) the partial combustion of the vapours produced, with the evolution of heat, whereby the carbon particles become white-hot and luminous; the access of air at this stage being insufficient for complete combustion; (3) the completion of combustion owing to admixture with an excess of air, producing great heat but little light. The phenomena of flame are dependent on the nature of the hydrocarbons supplied, on the heat generated within the flame, and on the air-supply.

A few experiments will easily show us that modification of the conditions has considerable influence on the nature of flame.

Exp. 96.—Introduce the nozzle of a blowpipe into the dark central zone of a candle, and direct a current of air into that area. By so doing we bring a supply of air into the heart of the flame sufficient to secure complete combustion, and we do it in such a manner that it becomes intimately mixed with the hydrocarbons.

The conditions necessary for the production of a luminous zone are no longer present, and in the resulting flame, the "blowpipe flame," we have two zones only, and in both the luminosity is feeble. The inner zone (see Fig. 31) contains excess of hydrocarbon over air, and the outer zone contains excess of air over hydrocarbon.

Similar phenomena are to be observed in the non-luminous flame of a Bunsen burner. Here the air is admitted by the holes at the base of the burner, and intermingles with the gas supplied from a small jet at the same level, so that the flame is the result of the combustion of an intimate mixture of gas and air, just as in the case of the blowpipe flame.

Exp. 97.—Make a short coil of stout copper wire by giving it half-a-dozen turns round a piece of glass rod about 5 m.m. in diameter, and so that only a small space is left between one coil and the next. Bring the coil into the upper part of the luminous zone of a candle flame; the flame will become smoky: if it be quickly depressed to the level of the wick, the flame loses its luminosity, and indeed may be extinguished altogether. Copper, being a good conductor and radiator, carries off heat and lowers the temperature to such an extent that the particles no longer maintain the white heat which imparts the luminosity to the flame, and the combustion is rendered so incomplete that carbonaceous matters escape combustion and pass off as smoke. The vapours may in this way be cooled down even below their point of ignition, and the flame is then extinguished altogether.

Oxidizing and reducing flames.—The foregoing paragraphs show that heated hydrocarbon vapours have the power of combining with oxygen in the gaseous condition to form carbon monoxide or dioxide and water vapour. They have also the power of abstracting oxygen from many solid oxides or bodies containing oxygen. This property may readily be shown either by means of the flame of a Bunsen burner or of the blowpipe.

Exp. 98.—Partially close the holes at the base of the Bunsen burner until there appears a well-defined luminous tip (A in Fig. 33) within the flame. Now introduce within the luminous area a small amount of barium sulphate on a loop of thin platinum wire, and hold it steadily there for two or three minutes.

The substance will be found to have changed in character, for whilst the barium sulphate originally taken is unacted upon by hydrochloric acid, the resulting body when moistened with dilute hydrochloric acid evolves an odour of sulphuretted hydrogen. The sulphate of barium ($BaSO_4$) has been deprived of its oxygen, and has become barium sulphide (BaS); this on treatment with dilute hydrochloric acid is transformed into the soluble chloride of barium with the evolution of H_2S—

$$BaS + 2\,HCl = BaCl_2 + H_2S.$$

Similarly, oxide of lead or copper may be reduced to metallic lead or copper when brought into the inner flame of the blowpipe (Fig. 32). In whatever part of a flame the hydrocarbons predominate and the supply of oxygen is limited, such a *reducing* action prevails. And wherever in a flame the supply of oxygen is in excess of that required to consume the hydrocarbons, as in the outer zone of the candle or the Bunsen burner or the blowpipe

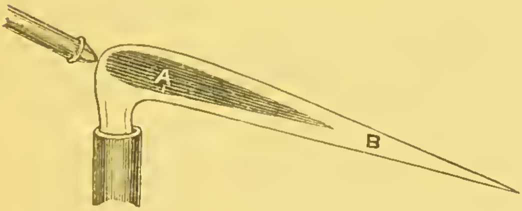

Fig. 32.

In Fig. 33
A is reducing area
BCD is oxidizing area
B low temperature oxidizing area
C high ,, ,, ,,

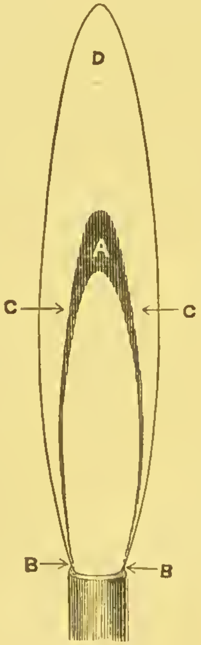

Fig. 33.

flame, an *oxidizing* action is experienced. This may be shown by bringing metallic tin or other metals into the outer margin of the Bunsen flame. The accompanying diagram (Fig. 33) illustrates the structure of the Bunsen flame with especial regard to the oxidizing and reducing areas, and to the temperature of the different parts of the flame.

SUMMARY.

(1) The nature of "fuel"—wood, coal and petroleum as fuels.
(2) The character of flame and the conditions that must be fulfilled in order that a gas or vapour may burn.
(3) *Special flames.*—
  The candle-flame (*a*) the zone of distillation.
    (*b*) ,, ,, incomplete combustion.
    (*c*) ,, ,, complete combustion.
  The flame of the Bunsen burner and the blow-pipe considered
    (*a*) in regard to temperature;
    (*b*) ,, ,, oxidizing or reducing action.

QUESTIONS.—CHAPTER XVI.

1. Describe the chemical changes which take place during the combustion of coal in a furnace.
2. What is the unit adopted for the measurement of heat? What volume of water may be raised from 10° C. to 50° C. by the heat derived from the combustion of 10 grammes of hydrogen and 10 grammes of carbon respectively?
3. What are the chief differences between lignite and peat, and between anthracitic and bituminous coal? Why does a pound of petroleum give out more heat during combustion than a pound of coal?
4. What conditions must be fulfilled in order that flame may be produced from coal, petroleum, and coal gas respectively?
5. Under what conditions is combustion accompanied by explosion? Three mixtures of coal gas and air are made and a light applied to each; one does not ignite at all, the second explodes, and the third burns quietly with a luminous flame. Explain these phenomena.
6. Sketch the flame of a candle showing the boundaries of the different zones of combustion.
7. Mention ~~the~~ chief constituents in the different zones of a candle flame.
8. In what respects does the blowpipe flame differ from the flame of a candle?
9. What is meant by the temperature of ignition of a gas? Explain the principle of the Davy lamp.
10. Give a diagram of the Bunsen flame, and indicate on it
    - (*a*) the reducing area;
    - (*b*) the oxidizing area;
    - (*c*) the high temperature oxidizing area;
    - (*d*) the low temperature oxidizing area.
11. How may calcium sulphate be reduced to calcium sulphide
    - (*a*) in the blowpipe flame;
    - (*b*) in the Bunsen flame?

CHAPTER XVII.

OXIDES OF CARBON.

CARBON MONOXIDE, CO, occurs in small quantity in chimney gases, especially where the air-supply during combustion is not in sufficiently large excess ; it is also formed during the dry distillation of wood, coal, and such organic bodies. The gases from blast or other furnaces in which an excess of carbon is present, and in which a reducing operation is being performed, consist largely of carbon monoxide.

Preparation.—The gas is usually prepared on the small scale in the laboratory by the action of concentrated sulphuric acid on oxalic acid, an equal volume of carbon dioxide being given off at the same time.

Exp. 99.—About 20 grammes of crystallized oxalic acid are put into an 8-ounce flask provided with thistle funnel and delivery-tube, and as much concentrated sulphuric acid as to cover it. Heat is applied steadily until effervescence sets in, and then moderated so as to secure a regular and not too rapid evolution of the gas. Collect over water, avoiding any escape of the gas, as it is very poisonous. The reaction which takes place is—

$$\left.\begin{matrix}\mathrm{COOH}\\ \mathrm{COOH}\end{matrix}\right\} + H_2SO_4 = CO + CO_2 + H_2O + H_2SO_4.$$

The sulphuric acid removes the elements of water from the oxalic acid without itself undergoing any chemical change.

Exp. 100.—Pour lime-water into a jar of the gas, and shake up ; the lime-water will become turbid owing to the formation of calcium carbonate[1]—

$$CaO + CO_2 = CaCO_3.$$

The presence of carbon dioxide is thus indicated.

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[1] After the experiment has been performed, it is well to burn the gas rather than to let it escape directly into the air.

Exp. 101.—Pour a few cubic centimetres of caustic soda into a jar of the gas and shake up well, the carbon dioxide will combine with the caustic soda, forming sodium carbonate—

$$2\,NaOH + CO_2 = Na_2CO_3 + H_2O.$$

Bring the mouth of the jar under water, the water will rise, and it will be seen that about half the volume of the gas is left. This is the carbon monoxide. Transfer some of this gas to a smaller vessel by decanting it over water, and shake up with lime-water; no turbidity will be produced,. the carbon dioxide having been removed. Now apply a light to the gas; it will burn with a beautiful blue lambent flame. When the combustion is finished, again shake up the vessel, and marked turbidity will then be produced, showing that carbon dioxide has again appeared. The carbon monoxide has united with oxygen during the process of combustion, with the formation of carbon dioxide—

$$2\,CO + O_2 = 2\,CO_2.$$

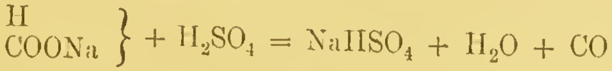
It may also be noticed that carbon monoxide does not itself support combustion, for if whilst it is burning the lighted taper be plunged into the vessel, the flame will be extinguished.

Exp. 102.—Remove the carbon dioxide from a second jar of the collected gas, and then decant into the jar sufficient air to fill the vessel.

We have now a mixture of equal volumes of carbon monoxide and air, and if after allowing the gases to stand for two or three minutes to mix properly, the mouth of the jar be held towards the flame of a Bunsen burner, it will be seen that carbon monoxide and air form an explosive mixture.

If it be desired to separate the carbon dioxide from the monoxide before collecting the gas this may be done by passing the gases evolved during its preparation through two wash-bottles containing caustic soda solution.

Carbon monoxide may, however, be prepared free from the dioxide by gently warming a mixture of sodium formate and sulphuric acid—



$$\left.\begin{matrix}H\\COONa\end{matrix}\right\} + H_2SO_4 = NaHSO_4 + H_2O + CO$$

or by heating roughly-powdered potassium ferrocyanide with *concentrated*[1] sulphuric acid.

An interesting method whereby carbon monoxide may be obtained in large quantities, though in an impure condition, is to pass carbon dioxide over red-hot charcoal. The charcoal may conveniently be heated in an iron pipe by means of a combustion furnace, and the carbon dioxide evolved in a gentle stream by the action of hydrochloric acid on marble—

$$CO_2 + C = 2\,CO.$$

The carbon monoxide is either collected or burnt at a jet attached to the exit of the tube.

This method of formation may be observed in a coke or red-hot cinder fire, on the surface of which the blue flames of the burning gas may be seen. The air passing in at the base of the fire at the lower part of the grate unites with carbon, forming carbon dioxide, and this as it passes over the mass of red-hot carbon in the upper part of the grate is transformed into carbon monoxide. "Generator" gas, used in some manufacturing operations, consists largely of carbon monoxide, and is obtained by passing air over a high column of red-hot coke or anthracite.

Properties.—Carbon monoxide is a colourless, tasteless gas of a very poisonous nature. It is only very slightly soluble in water, 100 volumes of water at ordinary temperatures dissolving less than three volumes of the gas. It is also very difficult to condense, the liquid boiling under atmospheric pressure at $-190°$ C. Under ordinary circumstances, carbon monoxide burns in air, or may be exploded with oxygen in a eudiometer, forming carbon dioxide. But when the gases are *perfectly dried* by exposing them for a lengthened period to phosphorus pentoxide, sparks may be passed through the mixture without combination taking place. In this connection it may be mentioned also that bodies like carbon, sulphur, and phosphorus will not burn in oxygen or air if moisture be entirely removed. Owing to the readiness with which carbon monoxide combines with oxygen, it is a powerful reducing agent. It also combines directly with the vapour of sulphur, forming carbonyl sulphide (COS), and in sunlight with chlorine, forming carbonyl chloride ($COCl_2$), also known as phosgene gas.

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[1] *Dilute* sulphuric acid gives rise to the formation of hydrocyanic acid (HCN).

CARBON DIOXIDE, CO_2.—This gas is of more frequent occurrence than carbon monoxide. Its presence in air and water has already been mentioned, and also the part it plays in the animal and vegetable kingdoms. It is given off in large quantities from lime-kilns, in which the limestone ($CaCO_3$) is decomposed by heat into quicklime (CaO) and carbon dioxide. Processes of fermentation and putrefaction give rise to the gas. Whenever an explosion of fire-damp occurs in coal-mines carbon dioxide is formed in large quantities, and constitutes what the miners call the *after-damp* or *choke-damp*.

Preparation.—Carbon dioxide is usually prepared by the action of dilute hydrochloric acid on marble ($CaCO_3$). No heat is required, and the operation may be carried out in a flask or Woulff's bottle fitted with delivery-tube, the reaction being—

$$CaCO_3 + 2\ HCl = CaCl_2 + CO_2 + H_2O.$$

Although somewhat soluble in water, the gas is usually collected over water; being, however, much heavier than air, it may be collected by downward displacement. All carbonates, when treated with dilute hydrochloric acid, liberate carbon dioxide; many, such as limestone, liberate it when heated.

We have already seen that carbon dioxide is formed when carbon or compounds containing it are burnt in excess of air. If carbon compounds are heated to redness with oxide of copper, the whole of the carbon is transformed into carbon dioxide, and it is in this way that the amount of carbon in such compounds is estimated.

The following experiments, and that described in Chapter VIII, page 87, will illustrate the properties of carbon dioxide.

Exp. 103.—Fill a large beaker of three or four litres capacity by downward displacement with carbon dioxide which has been bubbled through water to remove hydrochloric acid, and plunge a taper into the gas; it will be immediately extinguished. Now detach a soap-bubble charged with air into the beaker, and it will be found to float on the surface of the heavier carbon dioxide. The density and other properties of the gas may further be illustrated by pouring it over a lighted candle, and thus extinguishing it, or by ladling out the gas with a smaller beaker, and showing the presence of carbon dioxide in the beaker by its extinguishing a taper.

Exp. 104.—Insert burning magnesium ribbon into another beaker of carbon dioxide; the combustion will continue at the expense of the oxygen in the carbon dioxide, and particles of carbon which are liberated will be observed on rinsing out the beaker with water. Carbon dioxide is a compound of great stability, but it may be decomposed by certain metals, such as magnesium or potassium, which have a very great affinity for oxygen.

Exp. 105.—Pass a stream of carbon dioxide through a few cubic centimetres of water to which some drops of litmus solution have been added, and note that the litmus assumes a claret tinge; contrast this with the effect of adding litmus to water containing a little hydrochloric or sulphuric acid. Notice also that by boiling, the carbon dioxide is expelled, and the litmus assumes its original colour. A solution of carbon dioxide in water is therefore very unstable, and possessed of a feebly acid character.

Exp. 106.—Pass the expired air from the lungs, or carbon dioxide (washed) from marble, through a slightly alkaline pink solution of phenol-phthalein; the pink liquid becomes colourless. This change from a pink to a colourless solution may be used as a means of indicating the presence of carbon dioxide.

Properties of carbon dioxide.—Carbon dioxide is a colourless gas with a very faintly acid taste. It is about $1\frac{1}{2}$ times as heavy as air; water at 15° C. dissolves about its own volume of the gas, at 0° C. 100 volumes of water dissolves 180 volumes of the gas. As with other gases, the amount dissolved increases directly as the pressure under which solution takes place, and soda-water being water charged with the gas under about four atmospheres pressure contains about four times its volume of the gas. Under a pressure of 36 atmospheres at 0° C. it condenses to the liquid form, and in this form it is prepared on a tolerably large scale and stored in steel cylinders. If the nozzle of one of these cylinders be opened, the pressure being released, the liquid is rapidly transformed into gas. The amount of heat absorbed by the passage from the liquid to the gaseous condition is considerable, and the issuing gas becomes so far cooled that a part of the gas condenses again even to the solid form. Solid carbon dioxide is a white, snow-like substance which passes only comparatively slowly into the gaseous condition again. The depression of temperature by its passage from the solid to the gaseous condition is such that mercury can be readily cooled down to – 40° C. and obtained as a solid body. Carbon dioxide, as will appear from the previous experiments, is in general a non-supporter of combustion or of animal life. It is decomposed by the green colouring-matter of plants in presence of sunlight, carbon being assimilated and oxygen set free in the process.

The carbonates.—We have seen in a previous paragraph that a solution of carbon dioxide in water shows a feebly acid reaction. For this reason, and from a consideration of the salts known as the carbonates, carbon dioxide is to be regarded as the anhydride of carbonic acid, and the composition of the acid, although never isolated, may be taken as H_2CO_3.

Carbonic acid has two atoms of hydrogen replaceable by metals, and is therefore a *dibasic* acid. In the acid carbonates or *bicarbonates* only half the hydrogen is so replaced, thus $KHCO_3$ is bicarbonate of potash, and $NaHCO_3$ is bicarbonate of soda. In the normal carbonates the whole of the hydrogen is replaced, as with K_2CO_3, potassium carbonate, and Na_2CO_3, sodium carbonate.

Exp. 107.—Pass carbon dioxide to saturation into a solution of caustic soda, and then evaporate down to dryness on a water-bath. A residue will be obtained consisting of the monohydrated normal carbonate of soda, $Na_2CO_3 . H_2O$.

Dissolve as much as possible of this in hot water and allow to cool, crystals of $Na_2CO_3 . 10\,H_2O$ will be formed. This is the product known as "soda crystals," and used as washing soda.

Very gently warm a quantity of this salt, or preferably the $Na_2CO_3 . H_2O$ in an atmosphere of carbon dioxide; it will take up CO_2 and be transformed into the bicarbonate, $NaHCO_3$—

$$Na_2CO_3 . H_2O + CO_2 = 2\,NaHCO_3.$$

Exp. 108.—Heat in a porcelain basin over the Bunsen flame a few grammes of dry bicarbonate of soda; carbon dioxide will be given off, and the normal carbonate again reproduced—

$$2\,NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The carbonates and bicarbonates of the alkalies are obtained by means of such reactions; they are soluble in water, whilst the carbonates of other metals are insoluble in water but soluble with decomposition in acids—

$$CaCO_3 + 2\,HCl = CaCl_2 + CO_2 + H_2O.$$

Some bicarbonates, *e.g.* $CaH_2(CO_3)_2$, are soluble in water (see p. 87).

The carbonates that are insoluble in water may be obtained (1) by the addition of alkaline carbonates to a soluble salt of the metal—

$$Na_2CO_3 + BaCl_2 = BaCO_3 + 2\,NaCl\,;$$

(2) by passing carbon dioxide into a solution of the hydrate—

$$CaH_2O_2 + CO_2 = CaCO_3{}^{1} + H_2O.$$

Weak bases such as alumina, oxide of silver, and oxide of mercury either form no carbonates or very unstable ones, and the normal carbonates of the alkalies are the only ones which withstand a high temperature without decomposition.

Test for carbonates.—Add dilute hydrochloric acid to the solid carbonate, or an aqueous solution of a carbonate in a test-tube. An effervescence will be observed, and on decanting the gas downwards into a second tube containing lime-water, and shaking up, a turbidity will be produced in the lime-water owing to the formation of calcium carbonate.

SUMMARY.

Carbon monoxide.

(1) *Preparation.*—

- (*a*) by the action of red-hot carbon on CO_2 or when carbon is burnt with an insufficient supply of air.
- (*b*) by the action of sulphuric acid on a formate.
- (*c*) „ „ „ oxalic acid.
- (*d*) „ „ „ potassium ferrocyanide.

(2) *Properties.*—

- (*a*) Very slightly soluble in water, poisonous.
- (*b*) Liquefied only under high pressure at very low temperature.

---

[1] Excess of CO_2 transforms this into the soluble bicarbonate—

$$CaCO_3 + H_2O + CO_2 = CaH_2(CO_3)_2.$$

(c) Combustible (forming CO_2) but not a supporter of combustion.

(d) Generally inert as a chemical agent, but under certain conditions it combines with oxygen, sulphur and chlorine.

Carbon dioxide.

(1) *Preparation.*—

(a) by burning carbon or carbonaceous substances in excess of air.

(b) by heating carbon or organic substances along with certain oxides.

(c) by the action of acids on carbonates.

(2) *Properties.*—

(a) Heavier than the air, non-supporter of life or of combustion.

(b) Dissolves in about its own volume of water at ordinary temperatures, solution faintly acid.

(c) Liquefies under moderate pressure.

(d) Chemically inert, decomposed with difficulty.

(e) Readily soluble in caustic alkalics forming carbonates.

(3) *Carbonates.*—formed by

(a) combination of CO_2 with oxides or hydroxides.

(b) precipitation of insoluble carbonates.

Many carbonates are decomposed by heat with evolution of CO_2.
All ,, ,, ,, acid ,, ,, ,,

QUESTIONS.—CHAPTER XVII.

1. Mention some conditions under which carbon monoxide is produced during the combustion of fuel on the large scale.
2. You desire to collect a specimen of CO as free as possible from air or CO_2, using oxalic acid as the source of the gas; how would you proceed?
3. How may CO be transformed into CO_2 and CO_2 into CO?
4. What experiments would you perform in order to distinguish between CO and CO_2?
5. What is the action of dilute and of concentrated sulphuric acid on potassium ferrocyanide?
6. What is "generator gas," and how is it made? How would you show that it contains (*a*) CO, (*b*) CO_2, (*c*) H?
7. It has been shown that chemical action undergoes modification when the reacting substances are perfectly dried; give instances of this.
8. Describe the reactions which take place when sodium bicarbonate ($NaHCO_3$) and lead carbonate ($PbCO_3$) are respectively subjected to the action of heat, and when they are brought into contact with dilute nitric acid.
9. Write down in separate columns (*a*) the physical, (*b*) the chemical properties of carbon dioxide.
10. Give two methods for the decomposition of carbon dioxide.
11. How are carbonates in general formed? Given metallic zinc, lime, and caustic potash, how would you prepare specimens of zinc carbonate, calcium carbonate, and potassium carbonate?

CHAPTER XVIII.

CHEMICAL CALCULATIONS.

I.—The relations between weight and volume of gases.

We have seen (Chapter VI.) that the densities of gases are proportional to their molecular weights. In order to express the weight of any gas it is convenient to remember as the basis of calculation that 1 *litre of hydrogen at the standard temperature* (0° *C.*) *and pressure* (760 *m.m. of mercury*) *is* 0·0899 *gramme*, or that 11·12 litres of hydrogen weigh one gramme.

If then we desire to ascertain the weight of any other gas under like conditions, we commence by expressing in chemical symbols the molecule of the gas thus—

The molecule	of	hydrogen	is expressed by	H_2	(2)
,,	,,	nitrogen	,,	N_2	(28)
,,	,,	oxygen	,,	O_2	(32)
,,	,,	chlorine	,,	Cl_2	(71)
,,	,,	ozone	,,	O_3	(48)
,,	,,	phosphorus	,,	P_4	(124)
,,	,,	water vapour	,,	H_2O	(18)
,,	,,	hydrochloric acid	,,	HCl	(36·5)
,,	,,	carbon dioxide	,,	CO_2	(44)
,,	,,	nitric oxide	,,	NO	(30)
,,	,,	sulphur dioxide	,,	SO_2	(64)
,,	,,	sulphuretted hydrogen	,,	H_2S	(34)
,,	,,	ammonia	,,	NH_3	(17)

and so on.

The relative weights are, then, those stated in parenthesis after the symbol in the above list, as derived from the respective atomic weights.

Thus the weight of a litre of nitrogen is 14 times that of a litre of hydrogen or (0·0899 × 14) grammes; a litre of carbon dioxide weighs (0·0899 × 22) grammes; a litre of sulphuretted hydrogen weighs (0·0899 × 17) grammes.

The alternative method of expressing the same facts is perhaps more readily applied in chemical calculations, viz. that 11·12 litres of hydrogen weigh 1 gramme or 22·24 litres (usually stated as 22·4) of hydrogen weigh 2 grammes, the same number of grammes as that used for expressing the molecular weight. In this form the statement is quite general, that the molecular weight being *m*, 22·24 litres of any gas whatever weigh *m* grammes.

22·24 litres of nitrogen	weigh	28	grammes.
22·24 ,, ,, oxygen	,,	32	,,
22·24 ,, ,, chlorine	,,	71	,,
22·24 ,, ,, sulphur dioxide	,,	64	,,
22·24 ,, ,, ammonia	,,	17	,,

It is convenient to remember both forms of the expression, as one or the other is more readily adapted for the purpose of calculation according to the terms which are given. For instance, if it be desired to calculate the weight of a certain volume of a gas, the former expression lends itself more readily for the purpose—as in the following example—

(1) Required the weight of 100 c.c. of carbon dioxide at 0° C. and 760 m.m. pressure—

1000 c.c. (1 litre) of hydrogen	weigh	0·0899	grammes.
,, ,, carbon dioxide	,,	1·9778	,,
100 cubic centimetres of ,, ,,	,,	0·19778	,,

Should the weight of the gas be given, and its volume is to be determined, the second form of expression is more easily applied.

(2) Required the volume occupied by 0·5 gramme of ammonia at 0° C. and 760 m.m. pressure—

17 grammes of ammonia	occupy	22·24	litres.
1 ,, ,,	,,	1·308	,,
0·5 ,, ,,	,,	0·654	,,

It is useful also to bear in mind that air is 14·435 times as heavy as hydrogen, since frequently the densities of vapours as actually determined by experiment are stated in terms of air as unit.

Thus the density of sulphur dioxide is found by experiment to be 2·247, air being the unit.

The density compared with hydrogen is therefore 2·247 × 14·435, or 32·43, a value agreeing well with that deduced from the accepted composition of this gas.

II.—Correction for temperature and pressure.

We shall first consider the influence of variations of *temperature* on the volume of a gas, and consequently on the weight of a given volume.

We have seen (Chap. VI.) that a gas at 0° C. expands $\frac{1}{273}$ of its volume for each increment of one degree Centigrade in temperature. The more general form of expression, viz. that the volume of the gas is proportional to the absolute temperature (see p. 49), will be found the most useful, as a few examples will show. In order to make the calculation it is in the first place necessary to convert the temperatures as ordinarily stated into absolute temperatures.

(3) A litre of gas is measured at 0° C.; what volume will it occupy at − 20° C., and what at 50° C.?

$$\begin{aligned} 0^\circ \text{ C.} &= 273^\circ \text{ absolute.} \\ -\ 20^\circ \text{ C.} &= 253^\circ \quad " \\ +\ 50^\circ \text{ C.} &= 323^\circ \quad " \end{aligned}$$

Volume required is at − 20° C. $1 \text{ litre} \times \frac{253}{273} = 926·8 \text{ c.c.}$

" " " + 50° C. $1 \text{ litre} \times \frac{323}{273} = 1183·2 \text{ c.c.}$

(4) The volume of a gas measured at 10° C. is found to be 150 c.c.; what volume would it occupy at the standard temperature (0° C.)?

$$10^\circ \text{ C.} = 283^\circ \text{ absolute.}$$

Volume required is at 0° C. $150 \times \frac{273}{283} = 144·7 \text{ c.c.}$

(5) The volume of a gas measured at 15° C. is found to be

250 c.c.; what volume would it occupy at − 15° C. and at 57° C. respectively?

15° C. = 288° absolute.
− 15° C. = 258° ,,
+ 57° C. = 330° ,,

$$\text{Volume required at } -15^\circ \text{ C.} = 250 \times \frac{258}{288} = 224{\cdot}0 \text{ c.c.}$$

$$\text{,, ,, ,, } +57^\circ \text{ C.} = 250 \times \frac{330}{288} = 286{\cdot}5 \text{ c.c.}$$

And now let us consider the effect of variation in *pressure*. According to Boyle's Law (see p. 51), the volume of a gas is inversely proportional to the pressure to which it is subjected when the temperature is constant.

(6) A gas measured at standard atmospheric pressure (760 m.m.) is found to occupy 1·5 litres; what volume will it occupy at 1,000 m.m. and at 100 m.m. pressure?

$$\text{Required volume at 1,000 m.m. is } 1{,}500 \times \frac{760}{1{,}000} = 1{,}140 \text{ c.c.}$$

$$\text{,, ,, ,, 100 m.m. is } 1{,}500 \times \frac{760}{100} = 11{,}400 \text{ c.c.}$$

(7) The volume of a gas at 500 m.m. pressure is found to be 250 c.c.; what would it measure under 5 atmospheres pressure?

5 atmospheres = (760 × 5) m.m. = 3,800 m.m.

$$\text{Required volume at 5 atmos.} = 250 \times \frac{500}{3{,}800} = 32{\cdot}9 \text{ c.c.}$$

Finally, an example is given of the allowance for both temperature and pressure in the same expression.

(8) A gas occupies 190 c.c. at 13° C. and 740 m.m. pressure; what volume would it occupy at standard temperature and pressure (0° C. and 760 m.m.), and what at − 130° C. and 780 m.m. pressure?

13° C. = 286° absolute.
0° C. = 273° ,,

$$\text{Volume at } 0^\circ \text{ C. and 760 m.m.} = 190 \times \frac{273 \times 740}{286 \times 760} = 176{\cdot}6 \text{ c.c.}$$

− 130° C. = 143 absolute.

$$\text{Volume at } -130^\circ \text{ C. and 780 m.m.} = 190 \times \frac{143 \times 740}{286 \times 780} = 90{\cdot}1 \text{ c.c.}$$

III.—The relation between weight and volume of liquids and solids.

The specific gravity of liquids is expressed in terms of pure water at 15° C. as unit. The following table shows that the specific gravity of water varies at different temperatures, water at 4° being taken as 1.

Specific gravity of water at 0° = 0·99987
" " " 2° = 0·99997
" " " 4° = 1·00000
" " " 10° = 0·99975
" " " 15° = 0·99916
" " " 20° = 0·99826
" " " 25° = 0·99712

In ascertaining the density of a liquid by comparison with water it is more convenient to make the determination at ordinary temperatures, and hence it is usual to adopt the specific gravity of water at 15° C. as the basis of comparison.

When we say that the specific gravity of a liquid is 1·8 we mean that it is heavier than water in the proportion 1·8 : 1; if therefore 1 c.c. of water weighs 1 gramme, 1 c.c. of such a liquid will weigh 1·8 grammes.[1] The following examples will show how specific gravity of liquids enters into chemical problems.

(9) What is the weight of 100 c.c. of sulphuric acid of sp. gr. 1·84?

100 c.c. of water weigh 100 grammes.
" " sulphuric acid of the density given " 184 "

(10) Hydrochloric acid of sp. gr. 1·112 contains 21 per cent. by weight of gaseous hydrochloric acid; find the volume of hydrochloric acid gas in 10 c.c. of such acid.

By the method used in the previous problem 10 c.c. of hydrochloric acid will weigh 11·12 grammes.

$\frac{11{\cdot}12 \times 21}{100} = 2{\cdot}3352$ grammes, the weight of gaseous hydrochloric acid contained in it.

---

[1] This is not strictly accurate, since the gramme is the weight of 1 c.c. of water *at* 4° C. The correction, however, is only made in case a very exact expression is desired, and for ordinary purposes it is omitted. In any case the actual weight may be obtained by multiplying the result by 0·99916.

36·5 grammes of HCl occupy 22·32 litres;

$$2{\cdot}3352 \text{ grammes occupy } \frac{22{\cdot}32 \times 2{\cdot}3352}{36{\cdot}5} \text{ litres;}$$

$$= 1{\cdot}428 \text{ litres.}$$

The relation between weight and volume of solids, like that of liquids, is expressed in terms of water as unit. Thus, diamond is 3·5 times as heavy as water, and its sp. gr. is 3·5, the sp. gr. of graphite is 2·2, of mercury 13·6.

The weight of these bodies that occupy the same volume as 1 gramme of water (that is, 1 c.c.) is 3·5, 2·2, and 13·6 respectively.

This relation is seldom necessary in chemical calculations.

IV.—Calculation of the percentage composition of a body.

When the chemical composition of a body is expressed by symbols, the proportions of the respective elements contained in it are the weights of the elements as determined from the table of atomic weights.

HCl indicates a compound formed by the union of 1 part by weight of hydrogen with 35·5 parts by weight of chlorine.

H_2O indicates a compound formed by the union of 2 parts by weight of hydrogen with 16 parts by weight of oxygen.

CO_2 indicates a compound formed by the union of 12 parts by weight of carbon with 32 (*i.e.* 2 × 16) parts by weight of oxygen.

P_2O_5 indicates a compound formed by the union of 62 (*i.e.* 2 × 31) parts by weight of phosphorus with 80 (*i.e.* 5 × 16) parts by weight of oxygen.

H_3PO_4 indicates a compound formed by the union of 3 parts by weight of hydrogen, 31 parts by weight of phosphorus, and 64 (*i. e.* 4 × 16) parts by weight of oxygen.

36·5	parts by weight of	HCl	contain	1	pt. of	H and 35·5	pts. of	Cl.
18	,, ,,	H_2O	,,	2	,,	H and 16	,, ,,	O.
44	,, ,,	CO_2	,,	12	,,	C and 32	,, ,,	O.
142	,, ,,	P_2O_5	,,	62	,,	P and 80	,, ,,	O.
98	,, ,,	H_3PO_4	,,	3	,,	H, 31 of P and 64 of O.		

The *percentage* composition is merely the statement of the relative weights of each of the constituents in 100 *parts* of the compound.

Thus, if 18 parts by weight of water contain 2 parts of hydrogen and 16 parts of oxygen, then 100 parts of water will contain—

$$\frac{2 \times 100}{18} \text{ parts of H, } i.e. \ 11{\cdot}11;$$

$$\text{and } \frac{16 \times 100}{18} \quad \text{,,} \quad \text{,,} \quad \text{O, } i.e. \ 88{\cdot}88;$$

and this represents the percentage composition of water.

(11) Find the percentage composition of potassium chlorate, $KClO_3$—

$$\begin{aligned} K &= 39{\cdot}1 \\ Cl &= 35{\cdot}5 \\ O_3 &= \underline{48{\cdot}0} \\ & 122{\cdot}6 \end{aligned}$$

$$\begin{aligned} \text{Percentage amount of K} \quad & \frac{39{\cdot}1 \times 100}{122{\cdot}6} = 31{\cdot}89 \\ \text{,,} \qquad \text{,,} \qquad Cl = & \frac{35{\cdot}5 \times 100}{122{\cdot}6} = 28{\cdot}95 \\ \text{,,} \qquad \text{,,} \qquad O = & \frac{48 \times 100}{122{\cdot}6} = \underline{39{\cdot}16} \\ & \qquad\qquad\quad \underline{\underline{100{\cdot}00}} \end{aligned}$$

(12) Find the percentage amount of water of crystallization in $FeSO_4 . 7 H_2O$.

$$\begin{aligned} Fe &= 56 \\ S &= 32 \\ O_4 &= 64 \\ 7\,H_2O &= \underline{126} \\ & 278 \end{aligned}$$

278 parts of $FeSO_4 . 7 H_2O$ contain 126 parts of water.

$$\text{Percentage of water} = \frac{126 \times 100}{278} = 45{\cdot}32.$$

The question which even more frequently arises in practice is the converse one, the determination of the formula of a substance from the results of analysis of the substance. We have seen already that the relative composition by weight of a body is obtained by taking the atomic weight of each constituent, and where more than one atom of any constituent is present, then the multiple of that according to the number of atoms.

E.g., for $COCl_2$—

	Atomic weight.	No. of atoms.	Product.	Percentage composition.
C	12	1	12	12·12
O	16	1	16	16·16
Cl_2	35·5	2	71	71·72

We now reverse the process, and desire to determine the relative number of atoms of each element, having given the composition by weight of a body as deduced from its analysis—

S = 23·7 per cent.
O = 23·7 „ „
Cl = 52·6 „ „

Let n, n', n'' be the number of atoms of S, O, and Cl respectively, the atomic weights being 32, 16, and 35·5, we have the relative weights of each of the constituents—

$$32\,n,\ 16\,n',\ \text{and}\ 35{\cdot}5\,n''.$$

These values are proportional to the weights as represented by the percentage composition, viz.—

23·7, 23·7, 52·6.

Thus—

$32\,n \propto 23{\cdot}7$ and n is proportional to 0·74.
$16\,n' \propto 23{\cdot}7$ „ n' „ „ 1·48.
$35{\cdot}5\,n'' \propto 52{\cdot}6$ „ n'' „ „ 1·48.

The *simplest proportion in whole numbers* is—

1 : 2 : 2,

and the formula on this assumption is—

$$SO_2Cl_2.$$

This, then, is the *empirical formula* as deduced solely from the consideration of the results of the analysis. It is quite consistent with such a calculation that the formula should be $S_2O_4Cl_4$, or $S_3O_6Cl_6$, or any such multiple. Which of these is to be finally accepted can only be decided after a determination of the vapour density of the body, or of its chemical constitution and character, and this would be the *constitutional formula* of the body.

To determine the empirical formula of a body, we therefore divide the results of analysis by the respective atomic weights, and the numbers so obtained are *proportional* to the number of atoms.

(13) The percentage composition of a compound is found to be H = 5·88 and O = 94·12: find its formula.

In this case n and n_1 being in proportion to the number of atoms of hydrogen and oxygen respectively

$$n\text{H} = 5{\cdot}88, \text{ and H being } 1,\ n = 5{\cdot}88.$$
$$n_1\text{O} = 94{\cdot}12, \text{ and O being } 16,\ n_1 = 5{\cdot}88.$$

The body therefore consists of an equal number of atoms of H and O, and the simplest formula would be HO. Chemical considerations, however, compel us to accept a multiple of this, viz. H_2O_2, as the formula of hydrogen peroxide, the substance whose composition had been ascertained.

(14) Find the formula of a substance having the composition—

Mg = 9·76.
S = 13·01.
O = 26·01.
Water of crystallization = 51·22.

$$\text{Mg gives } \frac{9{\cdot}76}{24} = 0{\cdot}406 \text{ as proportional number.}$$
$$\text{S} \quad ,, \quad \frac{13{\cdot}01}{32} = 0{\cdot}406 \quad ,, \quad ,,$$
$$\text{O} \quad ,, \quad \frac{26{\cdot}01}{16} = 1{\cdot}626 \quad ,, \quad ,,$$
$$H_2O \quad ,, \quad \frac{51{\cdot}22}{18} = 2{\cdot}846 \quad ,, \quad ,,$$

From these numbers we deduce as the simplest whole numbers bearing the same relation to one another 1 : 1 : 4 : 7, and the simplest formula for the body is—

$$MgSO_4.7\,H_2O.$$

V.—Application to chemical problems.

We have now considered the fundamental calculations which enter into chemical problems, and a few examples will be given to show how these bear upon questions involving chemical decomposition and interchange.

(15) What weight of caustic soda (NaOH) will be needed to just neutralize 10 c.c. of dilute sulphuric acid (sp. gr. 1·155) containing 21 per cent. of H_2SO_4?

In all cases where a chemical reaction is concerned, involving considerations of weight or volume, it is well to state the reaction in the form of an equation at the outset—

$$2\,NaOH + H_2SO_4 = \underset{\text{Sodium Sulphate.}}{Na_2SO_4} + 2\,H_2O.$$

From this we see that 2 NaOH neutralize H_2SO_4, the respective weight relations being—

$$2\,(23 + 16 + 1) \text{ and } (2 + 32 + 64) \text{ or } 80 : 98.$$

80 parts by weight of caustic soda serve to neutralize 98 parts by weight of sulphuric acid.

Now determine the actual weight of sulphuric acid that is to be neutralized—

10 c.c. of the dilute sulphuric acid (sp. gr. 1·155) weigh 11·55 grms.

21 per cent. of this is H_2SO_4, *i.e.* $\frac{11{\cdot}55 \times 21}{100} = 2{\cdot}4255$ grammes.

Required amount of caustic soda is—

$$\frac{2{\cdot}4255 \times 80}{98} \text{ grammes, or } 1{\cdot}98 \text{ grammes.}$$

(16) What volume of oxygen collected at standard temperature and pressure (0° and 760 m.m.) is given off on heating 10 grammes of mercuric oxide?

$$2\,HgO = 2\,Hg + O_2.$$

First determine the *weight* of oxygen from the above equation, which shows that 432 parts of mercuric oxide yield 32 parts of oxygen, or, in simpler numbers, 27 parts yield 2 parts of oxygen.

10 grammes therefore yield $\frac{2 \times 10}{27}$, or 0·74 gramme.

Now 32 grammes of oxygen occupy at standard temperature and pressure 22·24 litres, and the *volume* of oxygen corresponding to this weight is—

$$\frac{0{\cdot}74 \times 22{\cdot}24}{32} = 514 \text{ cubic centimetres.}$$

(17) What weight of sulphur must be burnt so as to yield 1 litre of sulphur dioxide at standard temperature and pressure?

$$S + O_2 = SO_2.$$

Here we start from a known *volume* of gas and must work back to the *weight* in terms of which the result is to be expressed.

22·24 litres of SO_2 weigh 64 grammes.

1 litre of SO_2 weighs $\frac{64}{22·24}$ or 2·867 grammes.

Also 64 grammes of SO_2 contain 32 grammes of S,
and 2·877 „ SO_2 „ 1·4385 „ S.

1·4385 grammes of sulphur will therefore be required to produce 1 litre of SO_2.

Such a calculation may, however, be shortened by the consideration that as 32 grammes of sulphur, according to the equation, yield 64 grammes or 22·24 litres of SO_2,

$\frac{32}{22·24}$ grammes will yield 1 litre of SO_2.

The next example will be rendered more complex by introducing conditions of temperature and pressure differing from the standard. No further difficulty is really involved, except that the correction for temperature and pressure must be made.

(18) 2½ litres of nitrous oxide have been collected at 39° C. and 741 m.m. pressure; what weight of ammonium nitrate has been decomposed in order to supply the gas?

First eliminate the irregularity introduced by the temperature and pressure, by determining what volume the gas would have occupied had it been collected at standard temperature and pressure. This will be—

$$\frac{2·5 \times 273 \times 741}{312 \times 760} \text{ litres, or } 2·133 \text{ litres.}$$

Now according to the equation—

$$\underset{\text{Ammonium nitrate.}}{NH_4NO_3} = \underset{\text{Nitrous oxide.}}{N_2O} + 2\,H_2O.$$

80 grammes of ammonium nitrate yield 44 grammes (or 22·24 litres) of nitrous oxide, and hence

$\frac{80 \times 2·133}{22·24}$ grammes, or 7·673 grammes, of ammonium nitrate have been decomposed.

(19) One gramme of water is (*a*) converted into steam at 100° C., (*b*) decomposed by means of sodium and the hydrogen collected at 13° C.; what volume will each occupy, the barometer at the time standing at 750 m.m.?

First, let us consider the case of the steam. This being water vapour has, at standard temperature and pressure, a density such that, as previously shown,

18 grammes is the weight of 22·24 litres.

Thus 1 gramme occupies $\frac{22 \cdot 24}{18}$ or 1·235 litres.

At 100° C. and 750 m.m. pressure this occupies—

$$\frac{1 \cdot 235 \times 373 \times 760}{273 \times 750} = 1 \cdot 71 \text{ litres.}$$

Secondly, as to the hydrogen, the decomposition is represented by the equation—

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2;$$

from which we see that 36 grammes of water yield 2 grammes of hydrogen, and therefore 1 gramme of water yields $\frac{1}{18}$ gramme of hydrogen.

The *volume* of hydrogen at standard temperature and pressure is thus $\frac{11 \cdot 12}{18}$ or 0·62 litre. Corrected so as to represent the volume at 13° C. and 750 m.m. pressure this becomes—

$$\frac{0 \cdot 62 \times 286 \times 760}{273 \times 750} = 0 \cdot 658 \text{ litre.}$$

The whole of the more important elements entering into the treatment of chemical problems have now been discussed, and it only remains to add some examples in further illustration of their application to chemical reactions.

(20) 10 grammes of mercury are heated with excess of concentrated sulphuric acid and the sulphur dioxide formed is collected at 15° C. and 765 m.m. pressure; what volume does it occupy?

Here, as in most cases, it is best to commence by a statement of the reaction which takes place.

$$Hg + 2\,H_2SO_4 = \underset{\text{Mercuric Sulphate.}}{HgSO_4} + 2\,H_2O + SO_2.$$

200 grammes of mercury give 64 grammes of SO_2,
or 200 „ „ „ 22·24 litres of SO_2.
10 „ „ „ 1·112 „ „
at standard temperature and pressure.

Volume at 15° C. and 765 m.m. pressure is then

$$\frac{1 \cdot 112 \times 288 \times 760}{273 \times 765} = 1 \cdot 165 \text{ litre.}$$

(21) 25 c.c. of marsh gas (CH_4) are mixed with 500 c.c. of air and exploded in a eudiometer; what volume of gas should there be (*a*) before the removal of the carbon dioxide formed, (*b*) after the absorption of the carbon dioxide by means of caustic potash? The temperature and pressure may be assumed to be the same when each of the readings of volume were taken.

The chemical reaction which takes place is

$$\underset{2\text{ vols.}}{CH_4} + \underset{4\text{ vols.}}{2\,O_2} = \underset{2\text{ vols.}}{CO_2} + 2\,H_2O,$$

the nitrogen of the air taking no part in the combustion.

It is further manifest on inspection that the 2 volumes of marsh gas and 4 volumes of oxygen, before explosion, give rise to 2 volumes of carbon dioxide, the space occupied by the water being negligible.

Thus 6 volumes are reduced to 2, and the diminution is 4 volumes.

But the marsh gas occupies 25 c.c., and is represented by 2 volumes.

The diminution in volume is therefore 50 c.c., and the 525 c.c. of mixed gases originally present in the eudiometer have been reduced to 475 c.c.

Similarly the CO_2 occupies the same volume as the marsh gas from which it was obtained, and is thus 25 c.c., and if this be removed there will remain 450 c.c. of gas in the eudiometer. The result is that the residual gas—

(*a*) before removal of CO_2 is 475 c.c.
(*b*) after ,, ,, ,, 450 c.c.

(22) 10 c.c. of liquid carbon bisulphide (sp. gr. 2·63) are burnt in oxygen; find the volume of the resulting gases measured at standard temperature and pressure.

We must first ascertain the weight of the carbon bisulphide. Its sp. gr. being 2·63, the 10 c.c. will weigh 26·3 grammes.

The chemical change during combustion is represented in the equation

$$CS_2 + 3\,O_2 = CO_2 + 2\,SO_2.$$

76 grammes of CS_2 yield 44 grammes or 22·24 litres CO_2.
,, ,, ,, ,, 128 ,, ,, 44·48 ,, SO_2.
,, ,, ,, ,, 66·72 litres of CO_2 and SO_2 together.

26·3 grammes of CS_2 yield $\frac{66·72 \times 26·3}{76} = 23·09$ litres.

(23) Considering air as a mixture of 79 per cent. by volume of nitrogen with 21 per cent. by volume of oxygen, find the density of air compared with hydrogen. Also find the density of the vapour of carbon bisulphide compared with air.

79 vols. of nitrogen are as heavy as 79 × 14, or 1,106 vols. of H.
21 „ oxygen „ „ 21 × 16, or $\underline{\ 336}$ „ „
100 „ air „ „ 1,442 „ „

Density of air is 14·42.[1]

Density of the vapour of bisulphide of carbon is $\frac{12 + 64}{2}$ or 38, compared with H.

Compared with air it is therefore $\frac{38}{14·42} = 2·635$.

Atomic weights to be used in the following calculations.

Hydrogen,	1.	Chlorine,	35·5.
Carbon,	12.	Potassium,	39.
Nitrogen,	14.	Calcium,	40.
Oxygen,	16.	Iron,	56.
Sodium,	23.	Bromine,	80.
Magnesium,	24.	Silver,	107·6.
Phosphorus,	31.	Antimony,	119·6.
Sulphur,	32.	Mercury,	200.

Lead, 206·4

---

[1] Actual density at normal composition is taken as 14·435.

QUESTIONS.—CHAPTER XVIII.

1. The volume of a permanent gas at 0° C. is 3 litres; at what temperature would it occupy 4 litres, the pressure remaining unaltered?
2. Two samples of gas occupy the same volume, but one is at − 20° C., and the other at 20° C.; what is their relative volume when both are at 0° C.?
3. The volume of a gas at 13° C. is 100 c.c.; find its volume at − 130° C., at − 13° C., and at 130° C.
4. A gas under standard atmospheric pressure measures 209 c.c.; what volume will it occupy under a pressure of $\frac{1}{10}$, $\frac{1}{2}$, 2, and $5\frac{1}{2}$ atmospheres respectively?
5. What volume will half a litre of gas measured at 750 m.m. pressure occupy when subjected to a pressure of 850 m.m. of mercury?
6. A rectangular vessel 10 c.m. long, 5 c.m. wide, and 3·5 c.m. deep, is filled with gas at 100° C. and 770 m.m. pressure; what volume will the gas occupy at standard temperature and pressure?
7. A sample of gas is collected in a eudiometer, and it is found that the level of the mercury in the eudiometer is 257 m.m. above that of the trough, also the height of the barometer at the time is 745 m.m.; under what pressure is the gas?
8. A sample of gas is collected at standard temperature and pressure, and the pressure is then doubled, and the temperature gradually raised until the volume of the gas is the same as it was originally; at what temperature does this occur?

9. Under how many atmospheres pressure will steam have the same density as water (1 c.c. weighs one gramme), if the contraction takes place in accordance with Boyle's law, and the temperature remains at 600° C. ?

10. If the temperature remains at zero, at what pressure will hydrogen have a density equal to 0·62 of that of water, this being the density found by Dewar for hydrogenium ?

11. One cubic centimetre of bromine (density 3·2) is transformed into vapour at 78° C. ; determine the volume occupied by the vapour.

12. The sp. gr. of pure nitric acid being 1·522, find the weight of 100 c.c. of it, and the volume that you must take to weigh 100 grammes.

13. What volume of such acid will be required to just neutralize 100 grammes of caustic potash (KOH), and what weight of potassium nitrate is formed ?

14. Calculate the percentage composition of calcium carbonate ; what percentage of carbon dioxide does it contain ?

15. Chlorine forms with water a solid hydrate, having the composition $Cl_2 . 8 H_2O$; calculate the percentage of hydrogen, chlorine, and oxygen contained in this body.

16. Find the empirical formula of a compound consisting of 46·66 per cent. of iron and 53·33 per cent. of sulphur.

17. An oxide of iron contains 72·3 per cent. of iron ; determine its empirical formula.

18. Determine the simplest formula for a salt having the following percentage composition—

Sodium,	29·36.
Phosphorus,	26·38.
Oxygen,	44·26.
	100·00.

19. A solution of caustic soda having the sp. gr. 1·32 contains 28·8 per cent. of NaOH ; what weight of sulphuric acid is required to be just sufficient to neutralize a litre of such a solution ?

20. What volume of sulphuretted hydrogen at 13° C. and 798 m.m. pressure is required to effect the complete precipitation of one gramme of corrosive sublimate, $HgCl_2$?

21. What weight of pure antimony sulphide, Sb_2S_3, should yield a litre of sulphuretted hydrogen collected at 10° C. and 760 m.m. pressure?

22. Determine the volume of chlorine required to convert 10 grammes of phosphorus into the pentachloride.

23. A gramme of common salt is dissolved in water and excess of silver nitrate solution is added; what weight of silver chloride should be precipitated?

24. Calculate (*a*) the volume, (*b*) the weight, of carbon dioxide in the air of a room 6 metres long, 4 metres wide, and 3 metres high, if there is 1 volume of this gas present per 1,000 volumes of the air.

25. Dumas determined the relative amounts of nitrogen and oxygen in air by passing it over heated copper. He found—

Weight of tube and copper before experiment,	120	grms.
,, ,, ,, ,, ,, after ,,	121·15	,,
,, ,, globe when exhausted	852	,,
,, ,, ,, and nitrogen	855·85	,,

From these numbers calculate the percentage composition of air by weight, and deduce its percentage composition by volume.

26. Dumas determined the composition of water synthetically by passing hydrogen over heated copper oxide, and found—

Weight of tube and copper oxide before experiment,	334·598	grs.
,, ,, ,, ,, ,, ,, after ,,	314·236	,,
,, ,, drying tubes before experiment ...	426·358	,,
,, ,, ,, ,, after ,, ...	449·263	,,

Calculate the percentage composition of water by weight.

27. Ten grammes of steam are passed over red-hot iron; what volume of hydrogen at 26° C. and 741 m.m. pressure will be obtained if one-third of the steam undergoes decomposition?

28. Fifteen cubic centimetres of ammonia are completely decomposed by electric sparks, and then 40 c.c. of oxygen are added and the mixed gases exploded; stato the gases present and the volume of each (*a*) just before exploding, (*b*) after exploding.

29. A mixture of 10 litres of oxygen with one litre of carbon dioxide is shaken up with 100 c.c. of water; determine the volume of each gas that will be dissolved—the barometer at the time standing at 760 m.m. and the thermometer at zero.
30. Make the same determination with a mixture of one litre of oxygen and 10 litres of carbon dioxide.
31. A litre of sea-water (sp. gr. 1·03) is evaporated to dryness, and found to leave as residue 36·4 grammes of salts; find the percentage of solid matter in the sea-water.
32. Given that a metre is equivalent to 39·37 inches, calculate the number of cubic inches in a litre, and the number of litres in a cubic foot.
33. Determine the percentage of carbon in cane-sugar ($C_{12}H_{22}O_{11}$) and the volume of carbon dioxide that results from the combustion of 0·2 gramme of sugar.
34. A mixture of 20 c.c. of ethylene and 200 c.c. of oxygen is exploded in a eudiometer; what volume of gas remains after the explosion, and what volume when the carbon dioxide is subsequently removed by absorption with potash?
35. What quantity of crystallized oxalic acid ($C_2H_2O_4 . 2 H_2O$), heated with excess of sulphuric acid, will yield 5 litres of gas at standard temperature and pressure?
36. If 50 c.c. of sulphuretted hydrogen be mixed with excess of chlorine, what volume of hydrochloric acid will be formed, and what weight of sulphur liberated?
37. A gramme of a substance containing carbon is heated with lead oxide, and found to form 10 grammes of metallic lead; what percentage of carbon was present?
38. What weight of iron must be dissolved in dilute sulphuric acid in order to yield sufficient hydrogen to fill a balloon having a capacity of 100 cubic metres?
39. Ten grammes of carbon are burnt in 1,000 litres of air (taken as consisting of 79 vols. of N and 21 of O) at 15° C. and 700 m.m. pressure; find the percentage of nitrogen, oxygen, and carbon dioxide in the air after the combustion is complete.

ANSWERS TO QUESTIONS.

Chap. vi.	4.	Increased one-half ; decreased one-fourth.
,,	5.	Increased one-third.
,,	10.	61023 cubic inches.
		9153·4 ,, ,,
,,	11.	145 grms.
		68·96 c.c.
,,	12.	11·12 litres.
		700 c.c.
,,	13.	14, 62, 149·8, 23·8, 79·8, 38, 14.
,,	14.	$2\ K + 2\ H_2O = 2\ KOH + H_2$.
		$2\ SO_2 + O_2 = 2\ SO_3$.
		$2\ NaCl + H_2SO_4 = Na_2SO_4 + 2\ HCl$.
		$2\ H_2O + 2\ Cl_2 = 4\ HCl + O_2$.
Chap. vii.	5.	11·205 of hydrogen.
		88·795 of oxygen.
Chap. viii.	3.	A will be 10° C. ; B will be 50° C.
,,	4.	4000, 8000.
,,	5.	19·95, 127·5.
,,	6.	449·75 44·975 1349·25
		225·25 22·525 675·75
Chap. x.	4.	0·1 grm.
,,	7.	0·005 grm., 0·04 grm.
,,	8.	28, 18·7 ; 63·2, 31·6 ; 8, 5·3.
Chap. xi.	9.	5660 c.c.
Chap. xiii.	4.	19·6.
,,	5.	22·97.
Chap. xv.	2.	3794 tons.
Chap. xvi.	2.	8550 c.c. 2020 c.c.

ANSWERS TO CHEMICAL CALCULATIONS IN

CHAPTER XVIII.

1. 91°.
2. 293 : 253.
3. 50 c.c., 90·9 c.c., 140·9 c.c.
4. 2090 c.c., 418 c.c., 104·5 c.c., 38 c.c.
5. 441 c.c.
6. 129·17 c.c.
7. 488 m.m.
8. 273° C.
9. 3,951 atmospheres.
10. 6,894 atmospheres.
11. 571·9 c.c.
12. 152·2 grammes ; 65·7 c.c.
13. 73·9 c.c. ; 180·4 grammes.
14. Ca = 40 per cent.
    C = 12 ,,
    O = 48 ,,
    44 per cent.
15. H = 7·44 per cent.
    Cl = 33·02 ,,
    O = 59·54 ,,
16. FeS_2.
17. Fe_3O_4.
18. $Na_6P_4O_{13}$.
19. 465·7 grammes.
20. 81·9 c.c.
21. 4·847 grammes.
22. 17·93 litres.
23. 2·446 grammes.
24. 72 litres ; 142·4 grammes.
25. Oxygen, 23 ; Oxygen, 20·7.
    Nitrogen, 77; Nitrogen, 79·3.
26. Hydrogen, 11·1.
    Oxygen, 88·9.
27. 4·123 litres.
28. (*a*) N = 7·5 c.c.
    H = 22·5 c.c.
    O = 40·0 c.c.
    (*b*) N = 7·5 c.c.
    O = 28·75 c.c.
29. Oxygen = 3·73 c.c.
    Carbon dioxide = 16·36 c.c.
30. Oxygen = 0·37 c.c.
    Carbon dioxide = 163·6 c.c.
31. 3·534 per cent.
32. 61·023 ; 28·317.
33. 42·1 per cent.
    ·157 litre.
34. 180 c.c. ; 140 c.c.
35. 14·39 grammes.
36. 100 c.c. ; 0·0719 gramme.
37. 29 per cent.
38. 251·8 kilogrammes.
39. Nitrogen, 79.00 per cent.
    Oxygen, 19·2 ,, ,,
    Carbon dioxide, 1·8 ,, ,,

APPENDIX.

THE volume of a moist gas having been measured at a given temperature and pressure it is necessary to first find what volume the *dry* gas would occupy at 0° C. and 760 m.m. pressure. Allowance must be made (see chap. vi.)

(*a*) for the temperature of the gas (*i. e.* of the room).

(*b*) for the pressure to which it is subject (that of the atmosphere at the time of the experiment).

(*c*) the tension of water-vapour.

This involves a somewhat complex calculation, and a table has therefore been drawn up to enable the student to make the correction by using the factor given in the table.

Thus suppose the temperature of the laboratory to be 10° C. and the atmospheric pressure 740 m.m.; the tension of aqueous vapour with which the gas is saturated is for 10° C., 9·1 m.m. Now if v is the volume of the moist gas as observed, then V the volume of the dry gas at 0° C. and 760 m.m. pressure is given by the expression—

$$V = \frac{v \times 273 \times (740 - 9.1)}{283 \times 760} = 0{\cdot}928 \text{ v.}$$

To deduce the volume of the dry gas at standard temperature and pressure from the observed volume it is therefore only necessary to *multiply this latter by the factor* 0·928 as taken from the table, and so for any other temperature or pressure.

Pressure.	10° C.	12° C.	14° C.	16° C.	18° C.	20° C.
730 m.m. ...	0·915	0·907	0·899	0·891	0·882	0·874
740 m.m. ...	0·928	0·920	0·911	0·903	0·895	0·886
750 m.m. ...	0·940	0·932	0·924	0·915	0·907	0·898
760 m.m. ...	0·953	0·945	0·936	0·928	0·919	0·910
770 m.m. ...	0·966	0·957	0·949	0·940	0·932	0·923

For intermediate temperatures or pressures, the value may be expressed with sufficient accuracy by taking the proportional mean, *e. g.*

for 10° C. and 745 m.m. we shall find 0.934
for 11° C. and 750 m.m. ,, ,, 0.936

If we desire to know the *weight* of the hydrogen liberated, the following table may be used. Taking the weight of a litre of dry hydrogen under standard conditions as 0.0899 grm. the table gives the weight of hydrogen in a litre of the moist gas collected at the temperature of pressure given.

Pressure.	10° C.	12° C.	14° C.	16° C.	18° C.	20° C.
730 m.m. ...	0·0823	0·0816	0·0808	0·0801	0·0793	0·0786
740 m.m. ...	0·0834	0·0827	0·0819	0·0812	0·0805	0·0797
750 m.m. ...	0·0845	0·0838	0·0830	0·0823	0·0815	0·0808
760 m.m. ...	0·0857	0·0850	0·0842	0·0834	0·0826	0·0819
770 m.m. ...	0·0868	0·0860	0·0853	0·0845	0·0838	0·0830

An example will make the method of using the table quite clear, and serve to indicate how readily the weight of hydrogen may be arrived at when its volume has been observed.

Thermometer 16° C.
Barometer 750 m.m.

Observed volume of gas, 120 c.c.
The factor under 16° C. and 750 m.m. is 0·0823.

$$\text{Weight of hydrogen} = \frac{0{\cdot}0823 \times 120}{1000} = 0{\cdot}00988 \text{ grm.}$$

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